Journal of The Electrochemical Society

Review—Recent Progresses in 4D Printing of Gel Materials

To cite this article: Kumkum Ahmed *et al* 2020 *J. Electrochem. Soc.* **167** 037563

Journal of The Electrochemical Society, 2020 **167** 037563

Review—Recent Progresses in 4D Printing of Gel Materials

Kumkum Ahmed,[1,*,z] MD Nahin Islam Shiblee,[2,*] Ajit Khosla,[2,] Larry Nagahara,[3,***] Thomas Thundat,[4,***] and Hidemitsu Furukawa[2]**

[1] *Graduate School of Engineering and Science, Shibaura Institute of Technology, Koto-ku, Tokyo 135-8548, Japan*
[2] *Soft and Wet Matter Engineering Laboratory (SWEL), Department of Mechanical Systems Engineering, Graduate School of Science and Engineering, Yamagata University, Yonezawa, 992-8510, Japan*
[3] *Department of Chemical and Biomolecular Engineering, Whiting School of Engineering, Johns Hopkins University, Baltimore, Maryland 21218, United States of America*
[4] *Chemical and Biological Engineering, University at Buffalo, New York 14260, United States of America*

4D printing is based on 3D printing technology with an added dimension, where the printed structure evolves as a function of time. Materials that are stimuli-responsive are used for 4D printing such as shape memory alloys and polymers etc. Once these materials are 3D printed, they can morph into complex geometries on being exposed to external stimuli such as heat, temperature, pH etc. Among various stimuli responsive materials, gels are of great interest to soft robotics community because of their toughness and flexibility. Designing of complex 4D printed gel objects that are preprogrammed to morph into otherwise unattainable geometries opens the door for numerous applications in every field of science and technology. This paper presents a comprehensive review of current trends, prospects and challenges in 4D printing of gel materials with a focus towards their applications in soft robotics and bionic devices.
 [DOI: 10.1149/1945-7111/ab6e60]

Manuscript submitted October 11, 2019; revised manuscript received December 24, 2019. Published February 6, 2020. *This paper is part of the JES Focus Issue on Sensor Reviews.*

At present, 3D printing technology is one of the most rapidly growing technology that offers noteworthy future aspects with numerous potential applications in science and engineering. After emergence of the concepts of 3D printing many materials, techniques and devices have been developed and commercialized widely with a view to achieve a total grasp in our daily life to advanced manufacturing systems.[1–6] Smart materials, Soft functional materials and multi-material composites have been also introduced with drastic progresses in implementation and many efforts have been dedicated to fabricate new materials with desired functionality by incorporating nanomaterials such as graphene, carbon nanotubes, and functionalized nanoparticles or biomaterials with existing 3D printing materials.[7–11] Although 3D printing has many advantageous aspects, it still suffers from rigid and static parts that cannot activate or transform shape right off the printing base. In order to build moving parts, such as hinges or actuators, multiple parts must be assembled together after printing process that is somewhat tedious and time consuming just like mechanical parts assembling in conventional mold process. Also, the conventional 3D structures may not avail the need for use in biomedicine. The recently developed 4D printing technology based on 3D printing but with the embedded ability of shape transformation may solve this challenge and more accurately mimic the dynamics of the native tissues and attain prescribed functionality.

While 3D printing technology has been used to develop static structures from digital computer aided design (CAD) data in 3D coordination while 4D Printing is an evolving area that demonstrates a radical shift in additive manufacturing/3D printing with the evolution of smart materials that can entirely change their sizes or shapes in response to external stimuli and can be utilized for sensors, and actuators. The combination of a customized smart material with 3D system has created the idea of 4D printing emphasizing time as fourth dimension. This technique offers a one-dimensional path from idea to reality focusing on specific implementation and functionality that can be created directly into the materials.[12–16] The fourth dimension described here is the transformation of materials over time, highlighting the fact that materials are no longer simply immobile, dead objects, rather, they are as smart as programmably operational and transformable. Shape transforming characteristics like shrinkage, expansion, bending or folding after printing is the main characteristic of 4D printing which can be stimulated by temperature, humidity, or solvents, as well as pH or light.[17–22]

4D printing offers a number of distinctive advantages over 3D printing that has the potential to prove the required capability and amplify widespread implementation. More specifically, 4D printing offers actuation, sensing and programmability implanted directly into a material without the dependence on external devices or electromechanical systems like wires, motors, and batteries thus allow researchers to implement micro/nano-actuators and/or smart devices.[12–16] The advantages of these systems also include reduction of the assembly time, cost, manual labor, defects, space and the number of components in an archetype or system.[16,23] Applications of 4D printing have been reported in various fields, such as biomedical devices, security, fabrication of precise patterned surfaces for optics, electronic devices, structures with multi-directional properties and soft actuators.[16–19] Soft robotics have become extremely popular in the recent years, trying to mimic biology by creating soft and stiff controllable devices especially for the medical community. In recent years, use of temperature changing materials (Shape Memory Alloy),[24,25] electroactive polymers,[26] elastomers operatable by pressurized fluids or gases,[27] chemical stimuli and light sensitive materials[28,29] aiming for soft robotic and biomedical field are gaining foremost interests among the researchers. Consequently, it is expected that many new possibilities and prospects are intended to appear in the near future as emergence of 4D printing technology will open-up numerous new possibilities. In this review paper, we have focused on the recent advances in the 4D printing mainly with the gel-based materials and highlighted the potential existing researches focusing on the soft robotics and biomedical field. In addition, we have discussed the limitations and challenging aspects of gel-based 4D printing and indicated the prospective pathway to overcome in order to bring this technology in all-embracing applied field.

Beginning of 4D Printing

Currently, 3D printing represents a board range of printing techniques including fused deposition modelling (FDM),

*Electrochemical Society Student Member.
**Electrochemical Society Member.
***Electrochemical Society Fellow.
[z]E-mail: ahmed.kumkum.j2@sic.shibaura-it.ac.jp

stereolithography (SLA), selective laser sintering (SLS), selective laser melting (SLM), electron beam melting (EBM), inkjet 3D printing (3DP), direct ink writing (DIW), etc.[30–32] where all of these methods can be utilized for 4D printing upon combination with smart materials or in a smart method. Even in 3D printing the study of intelligent or active materials are very popular, but the concept of 4D printing was established in the TED conference of 2012 by Skylar Tibbits.[7] Tibbits demonstrated how a static printed object transformed from a linear 2D shape to 3D wireframe over time. This marked the beginning of the fourth-dimension moment of the 4D printing conception. Since then, 4D printing is increasingly gained considerable attention from scientists and engineers of different disciplines and making advancement in all possible sectors of 3D printing including printing method, material and design. 4D printing is the process of building a physical object using 3D printing that reacts to stimuli from the natural environment or through simulated intervention, resulting in a physical or chemical change of state through time. Thus, both physical and chemical transformation might be substantial elements to be considered in 4D printing. Although 4D printing seems to be directly effective for 3D printing with smart materials having self-morphing ability, it has been revealed that a printed single and non-active-material structure can also deform itself over time by precisely and smartly controlling the composition distribution of a nonactive components. Here multi-material structures have been mainly focused due to their versatile shape morphing possibility.[33–38] Consequently, 4D printing now can be valid for the concepts where non-active materials can be transformable with combination with 3D printing under suitable conditions. In fact, any printing techniques that can formulate dynamic structures with adjustable shapes or functionalities can be categorized as 4D printing. Due to the extraordinary potential of 3D and 4D printing in applied field, every year the number of articles on 3D and 4D printing is rapidly increasing. Figure 1 shows the quantitative number of research articles in 3D and 4D printing since 2010 and 2014 respectively. From this simple data, it can be easily understandable that these technologies are on the verge of blooming and many more new achievements are on the way in the near future.

Materials for 4D Printing and Related Advancements

4D printing sector is still in its birth stage and it is continuously evolving. Researchers are working on the feasibility of different materials and continuously improving them so that they can be used in real world scenario. Materials such as thermoplastics, metals, and ceramics are extensively used for generating 3D object by conventional 3D printers.[30–32] However, most of these materials are not suitable to 4D printing because of their lack of response to external stimuli. Recently, more materials with functional properties have been printed using 3D printers by varying different printing methods and employing different variables such as nozzle types, temperature, and printing condition.[30–32] The proper choice of materials is, therefore, foremost essential in 4D printing. Shape memory polymers (SMPs)[39–42] and stimuli-responsive hydrogels[43–46] are the most popular classes of active materials used for 4D printing due to their highly responsive shape morphing capability upon triggering. Besides these, dielectric elastomers (DEs),[47] liquid crystal elastomers (LCEs)[39,48] and meta materials[49,50] are utilized in 4D printing very recently. 4D printed SMPs deals with structural modification and recovery in response to temperature, which have been established through complex mechanism of multiple or reversible shape switching. However, SMPs cannot completely replace hydrophilic gel materials due to the limitations arising from their sustainability in wet environments, rigidity, material permeability, and biological compatibility.[51] Therefore, mechanically active, self-morphing gel materials that undergo programmable 3D shape transformations and perform mechanical tasks under an external trigger have recently attracted growing interest in the field soft robotics. The use of a hydrogel system in soft robotic counterparts proposes multiple advantages including simple designs, low cost, processability at low temperatures and in aqueous environments, and the possibility to mimic bioinspired function.[52–56] However, there is a lack of focussed review articles on the functionalities, potential and recent updates of gel-based soft materials towards 4D printing. Therefore, in this review article, we will extensively focus on the possibility of gel materials in 4D printing with proper elaboration of their future prospects and grand challenges. 4D printing of gel-based materials can be achieved by printing a single/multi-material structure followed by shape morphing due to swelling, pH or temperature induced volume transformation or by triggering through light, electric field etc. Here, we will further portray the potential and designability of gel material for 4D printing from the perspective of soft robotic and biomedical aspects.

4D Printing with Gel based System for Soft Machine Development

Guided movement of hydrogels can be obtained by expansion/contraction, for example, by isotropic volume expansion or shrinkage of homogeneous hydrogels or by the bending/unbending approach, which represents an anisotropic deformation and often involves construction of a hydrogel structure with two layers of different materials having different swellability values.[57–60] Multi-material printing, thus gaining much attention and thought to be the major contributor in establishing the core concept of 4D printing. Swelling induced 4D printing shows intelligent response of materials to their environment without the need of human contact. In extreme environmental conditions that is harsh for human such as in deep sea or during natural catastrophe these types of smart sensors and actuators could be of highly demanding in the year to come. Along with swelling, temperature controlling is another popular triggering method for 4D printing to activate the smart material for the purpose of shape morphing and constructing self-assembling origami.

The pioneering work on 4D printing presented by Tibbits and co-workers combined multi-material and their respective swelling properties to demonstrate 4D printing phenomena.[36,37,61] They designed a series of dynamic behaviour like linear stretching, ring

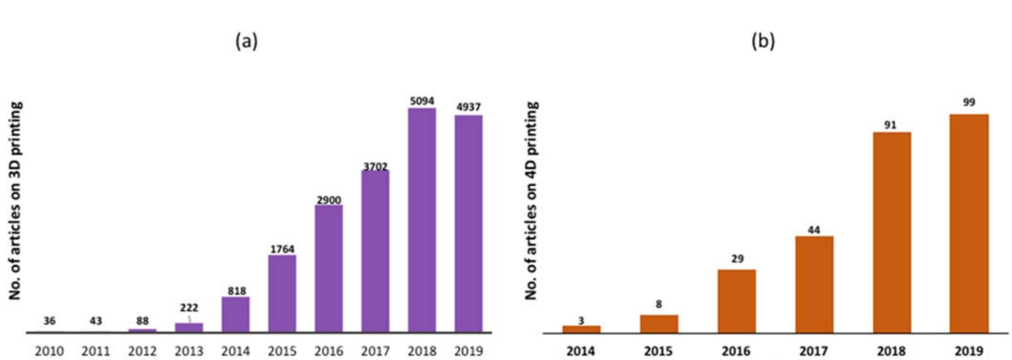

Figure 1. Number of articles on 3D and 4D printing (as of Sep 30, 2019. Source: Scifinder).

stretching, and folding with a rigid plastic base and a soft material that expanded upon exposure to water, using Stratasys Connex 500 printer. The expandable material was cross-linked hydrophilic polymer that formed a hydrogel when exposed to water, and in the process the printed gel experienced a large volume expansion up to 200%. They projected a combination of insights on both design and engineering aspect, and indicated that material programmability, multi-material printing techniques, and meticulous designs for accurate transformations are vital requirements for 4D printing. In an early demonstration on 4D printing by the team, the transformation of the printed grid structures was reported.[37] Materials capable of expanding to different degrees were used as the joints between two adjacent rigid segments, where the folding direction and angle of the joints could be controlled by regulating the material properties and tuning the position of the angle limiters. Subsequently, under suitable stimulus the printed grid could convert into the desired sinusoidal wave or hyperbolic surface (Fig. 2) or even time dependent complete transformation from MIT to SAL.

Bakarich et al. used a covalently cross-linked network of Poly(N-isopropylacrylamide) (PNIPAAm) that is thermally responsive.[38] It worked as the reinforcing agent and provide actuation through reversible volume alterations at critical temperature ($T_C = 32 \sim 35$ °C). They designed a new mechanically robust and thermo-responsive gel ink for 3D printing and printed a smart valve with full control of water using alginate/PNIPAAm based-ionic covalent entanglement (ICE) gel ink alongside other static materials. The valve automatically closed when exposed to hot water, dropping the flow rate by 99%, and reverse in cold water (Fig. 3). The alginate portion of the ICE gel resists the contraction of the thermally responsive PNIPAAm phase, so the contraction ratio decreased as the alginate fraction increased. The alginate/PNIPAAm ICE gels can be promising materials for developing soft-actuators because they can repetitively achieve a large free strain and blocked stress.

Naficy et al.[62] printed a hydrogel 3D architecture capable of reversible shape deformation in response to both hydration and temperature change. Polyether-based polyurethane (PEO-PU) has been incorporated into the matrix of a thermoresponsive poly(N-propylacrylamide) (NIPAm) and a non-responsive poly(2-hydroxyethyl methacrylate) (HEMA) based hydrogels where PEO-PU acted both as a rheology modifier and a swelling modifier. For construction of 3D structures, they used extrusion printing followed by UV exposure. They printed bilayer hinges composed of poly (NIPAm) and poly(HEMA) that can transform from a dry flat state to a controllably bended state when fully swollen below 32 °C due to the disproportional swelling of the two hydrogel layers during the hydration process (Fig. 4). By raising the temperature up to 60 °C, the deswelling of the poly(NIPAm) hydrogel occurred resulting in a new shape. Using this principle, they achieved a more complex cubic box exhibiting a reversible folding-unfolding behaviour stimulated by both hydration and temperature change.

Gladman et al. developed a biomimetic hydrogel composite that was 4D printed in bilayer structures with the ability to pattern in space and time and capable of shape changing when soaked in water due to localized swelling anisotropy.[63] The hydrogel composite ink was composed of stiff cellulose fibrils embedded in a soft acrylamide matrix similar to the composition of plant cell walls. The composite architectures were printed using a viscoelastic ink that contains an aqueous solution of N,N-dimethylacrylamide (pNNDMAm) (or N-isopropylacrylamide for reversible systems). During printing, when the ink flowed through the deposition nozzle the fibrils experienced shear-induced arrangement that lead to printed filaments with anisotropic toughness. Employment of anisotropic swelling allows accurate control over the curvature in bilayer structures which has been reported earlier.[49,64] They considered a theoretical model for a 3D structure produced by a set print path that prescribes the local orientation of the cellulose fibrils. They demonstrated independent control over both the mean and Gaussian curvatures, the two invariants connected with the curvature of any surface. They also printed a similar pattern using ink that lacked microfibrils and observed that it remained flat when swelled. The inter-filament

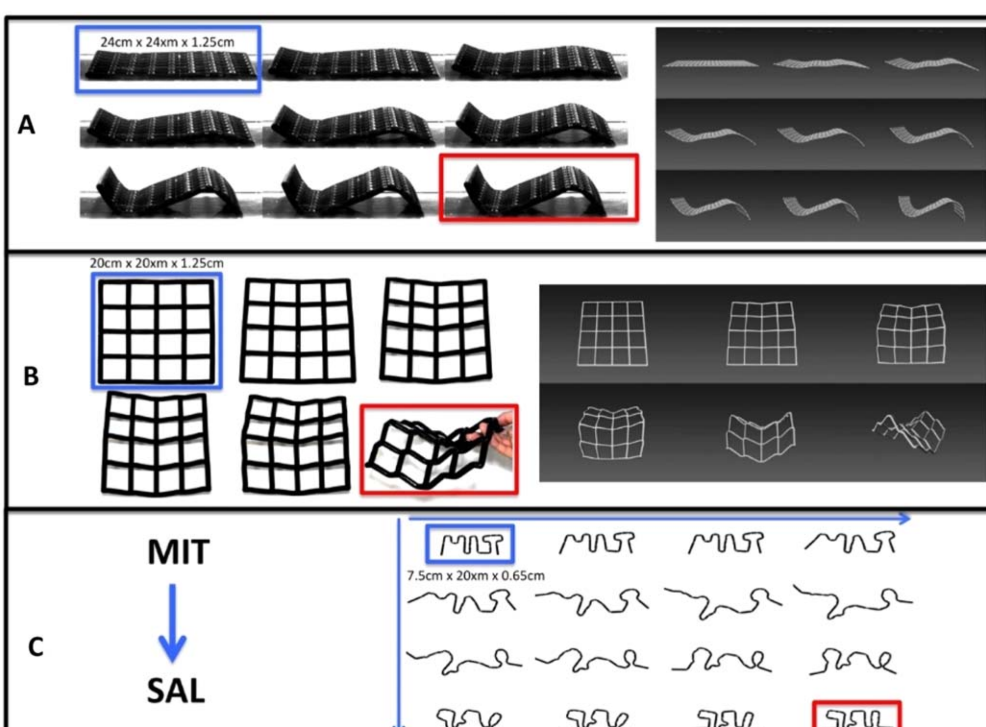

Figure 2. (a) Deformation of a grid into a sinusoidal wave. From left to right and top to bottom, we observe the grid as it folds into the desired shape. Only angular primitives were used. (b) Deformation of a grid into a hyperbolic surface. On the top, we visualize the fabricated model and, on the bottom, the simulated version. The final deformation provides a reasonable approximation despite using only folding bars in the simulation. (c) Fabricating a time-varying curve. From left to right and top to bottom, the curve deforms over time to a different shape. Reproduced with permission.[37] Copyright 2014 Springer Nature.

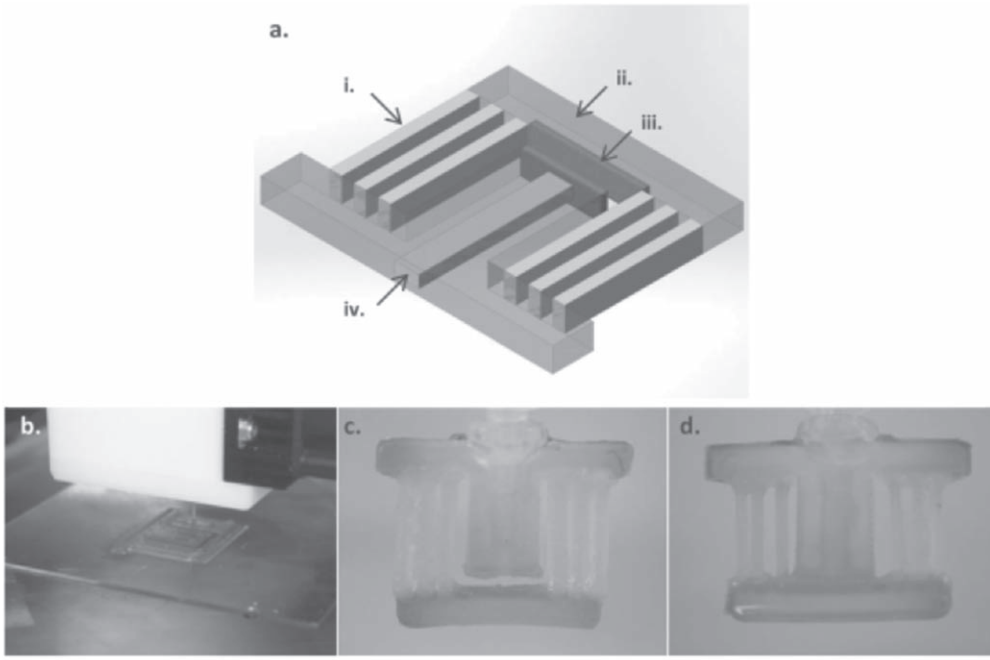

Figure 3. (a) Computer-aided design model of hydrogel valve. Labels indicate components to be printed with (i) alginate/PNIPAAm ICE hydrogel ink, (ii) Emax, (iii) alginate/polyacrylamide ICE hydrogel ink, and (iv) alginate-based ink for printing sacrificial support structures. (b) the Bioplotter printing the valve; (c) the 4D printed valve swollen in water at 20 °C; and (d) the 4D printed valve swollen in water at 60 °C. Reproduced with permission.[38] Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

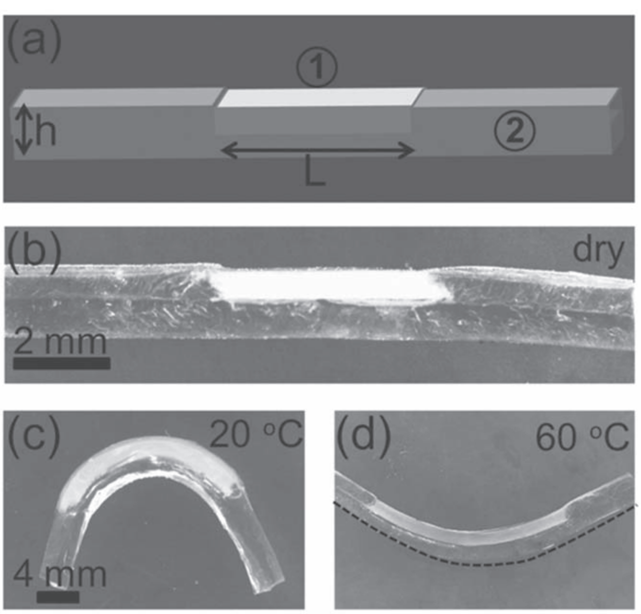

Figure 4. Hydrogel bilayers: (a) Schematic representation of a hydrogel hinge, made of the temperature-sensitive poly(NIPAM)-based top layer (1) and the poly(HEMA)-based PEO10-PU bottom layer (2). The fabrication parameters are h and L, as shown. Photograph of a hydrogel hinge shown in the dry state and (b) the same hydrogel hinge when fully swollen (c) at 20 °C and (d) 60 °C. Reproduced with permission.[62] Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

spacing helps the quick uptake of water through the filament radius (∼100 microns) that lead to shape alteration. They also printed a biomimetic structure of complex shaped Lilly flower in bio-4DP according to the print path (Fig. 5). By controlling some parameters such as filament size, orientation, and inter-filament spacing mesoscale bilayer architectures can be created that can alter their target shapes when immersed in water. Dicky et al. also utilized plant-inspired approach and demonstrated dynamic shape changing phenomenon of the printed hydrogel model upon immersion in water.[65] Although these works are one of the pioneering in the field of 4D printing using gel materials, the actuation speed and reversibility of these materials are very slow.

Huang et al. developed a printing setup containing computer-controlled projector and a reaction cell containing photo-curable monomer and revealed that with varying cross-linking densities, the sample response to water immersion differs resulting in a shape change in materials (Fig. 6).[66] They used photocurable acrylate based resin hydroxyethyl acrylate (HEA), hydroxyethyl methacrylate (HEMA) and potassium 3-sulfopropyl- methacrylate (PSPMA) where ionic PSPMA increased the swelling of the gel to create large stress. A digital projector in the visible light wavelength range has been utilized for curing process and found that longer exposure time results in a tighter cross-linking structure corresponding to a lower swelling ratio. They also demonstrated the shape memory effect using a hydrophobic shape memory polymer system in wax. Upon cooling the material to room temperature, the wax-swollen network turned into a rigid material due to the crystallization of the wax. The surface energy of the wax-like material along shape memory characteristics makes it useful for making morphable polymer parts. In contrary to typical layer by layer 3D printing process, the advantage of their system lies in the introduction of stresses into a printed 2D structure through a simple and easy way.

Recently self-folding structures have drawn significant attention due to their use in applications such as self- assembling, packaging, and medicine capsulation.[63,67,68] Mao et al. developed printed assemblies combining SMPs and hydrogels to construct 3D architecture that can reversibly switch between two rigid configurations.[69] The driving force for shape change comes from the swelling of the hydrogels, while the variation in temperature-activated modulus of the SMPs, controlled the time of such shape shifting. By regulating the temperature and water swelling condition, switching between two stable configurations without any mechanical loading and unloading was achieved. The idea was demonstrated in a trilayer strip with a reversible bending actuation behaviour. One of the limitations of such materials is that the whole actuation cycle require

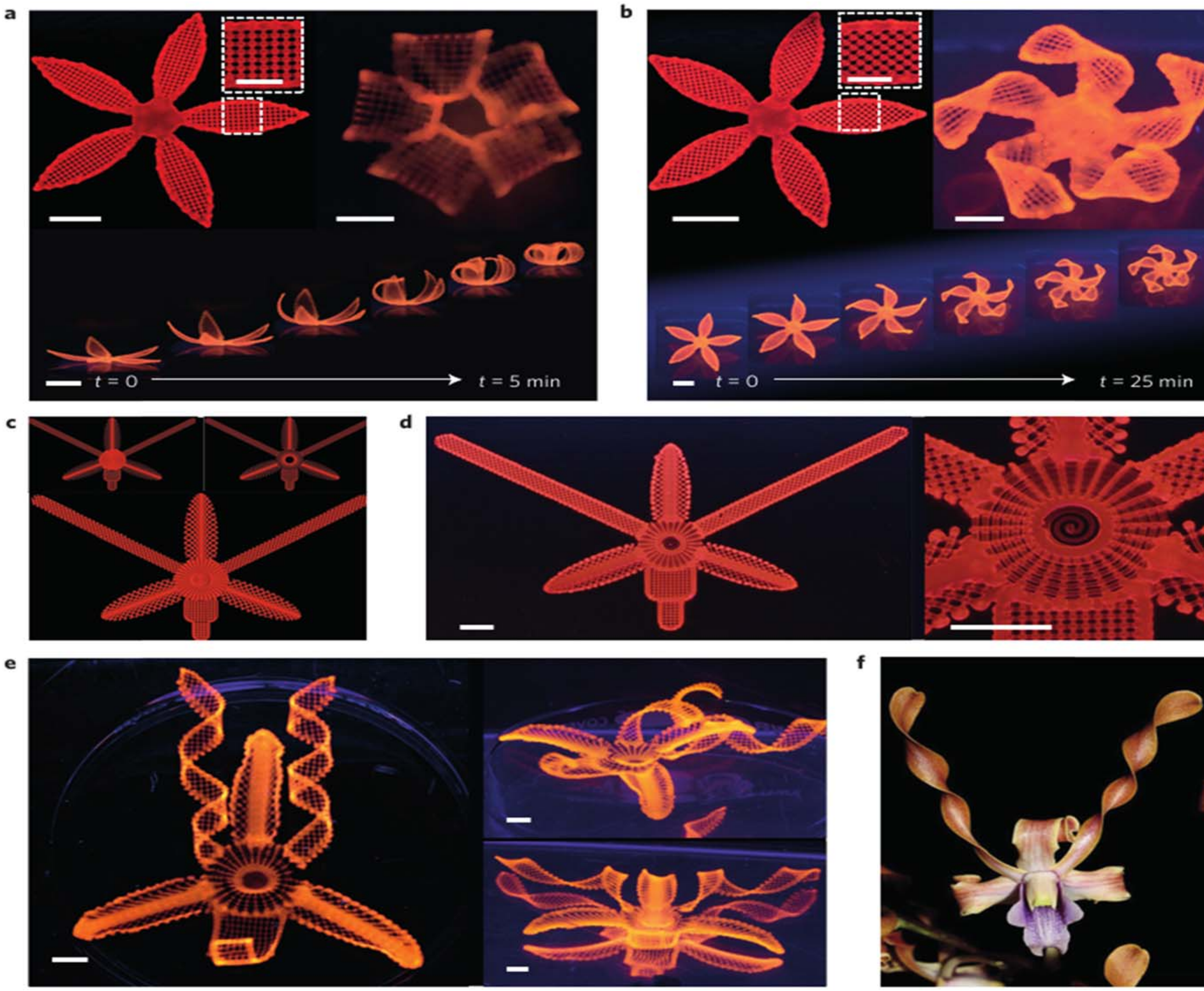

Figure 5. Complex flower morphologies generated by biomimetic 4D printing. a,b, Simple flowers composed of 90∘/0∘(a) and −45°/45°(b) bilayers oriented with respect to the long axis of each petal during the swelling process (bottom panel) (c), printed structure (d) and resulting swollen structure (e) of a flower demonstrating a range of morphologies inspired by a native orchid, the Dendrobium helix (courtesy of Ricardo Valentin) (f) Based on the print path, this orchid architecture exhibits four different configurations: bending, twisting and ruffing corolla surrounding the central funnel-like domain (scale bars, 5 mm). Reproduced with permission.[60] Copyright 2016, Springer Nature.

considerable time however might be suitable is systems where slow actuation is required in principal. Baker et al. demonstrated 4D printed origami-inspired structures by combining bilayers and trilayers (polyurethane hydrogel cores with polyurethane elastomer skins) within a single print.[70] A global trilayer composition (passive) with localised bilayer regions (active hinges) was formed to observe the shape-change upon hydration of the hydrogel and the change in shape was determined by the spatial location of the bilayers within the structure. They utilized commercial fused filament fabrication (FFF) based 3D printing process to fabricate these sandwich structures on a microscale using complex and exhibited an effective route of creating hydrogel-based origami structures (Fig. 7).

Shiblee et al. demonstrated soft bilayer actuator using two active layers composed of poly(N,N -dimethyl acrylamide-co -stearyl acrylate) (P(DMAAm-co-SA))-based Shape memory gels (SMGs) with different concentrations of the crystalline monomer SA within the gel network.[71] The printing was achieved by stereolithographic process by a customized optical 3D printer. The bending actuation properties from the “line-to-coil” shape and unbending in water and air were determined and effect of temperature, length and thickness on the actuation properties (deformation, reversibility, and response time) was thoroughly examined. They utilized two active layers of SMGs in the 4D printing process, wherein one layer predominates in terms of the high swelling degree and the other layer mainly influences the response time and recovery process in response to temperature. Finally, as a proof of concept, they demonstrated a nature-mimicking flower structure and an underwater 3D macroscopic soft gripper, that can grab, transport, and release a guest substance (Fig. 8). The underwater gripping and releasing phenomenon made this work particularly interesting as the system could operate repetitively without drying out the water. The applicability of these hydrogels in biomimetic actuators, encapsulating systems, and soft robotics may provide advantageous insights into the design of biomimetic smart systems with synergistic functions.

Motivated by the symmetrical and periodic tubular structures in biology, Liu et al. focused on the development of untethered, thermally responsive bioimplants and continuum robots. They reported the 4D printing of tube-like structures with alternating segmental patterns using active thermoresponsive gel (pNIPAM) and a passive thermally nonresponsive gel (polyacrylamide; pAAM) based on DIW[72] (Fig. 9). They demonstrated a variety of shape changes including uniaxial elongation, radial expansion, bending, and gripping based on two gels using finite element simulations. Mimicking the structural anatomy of the coral Polyp, they designed

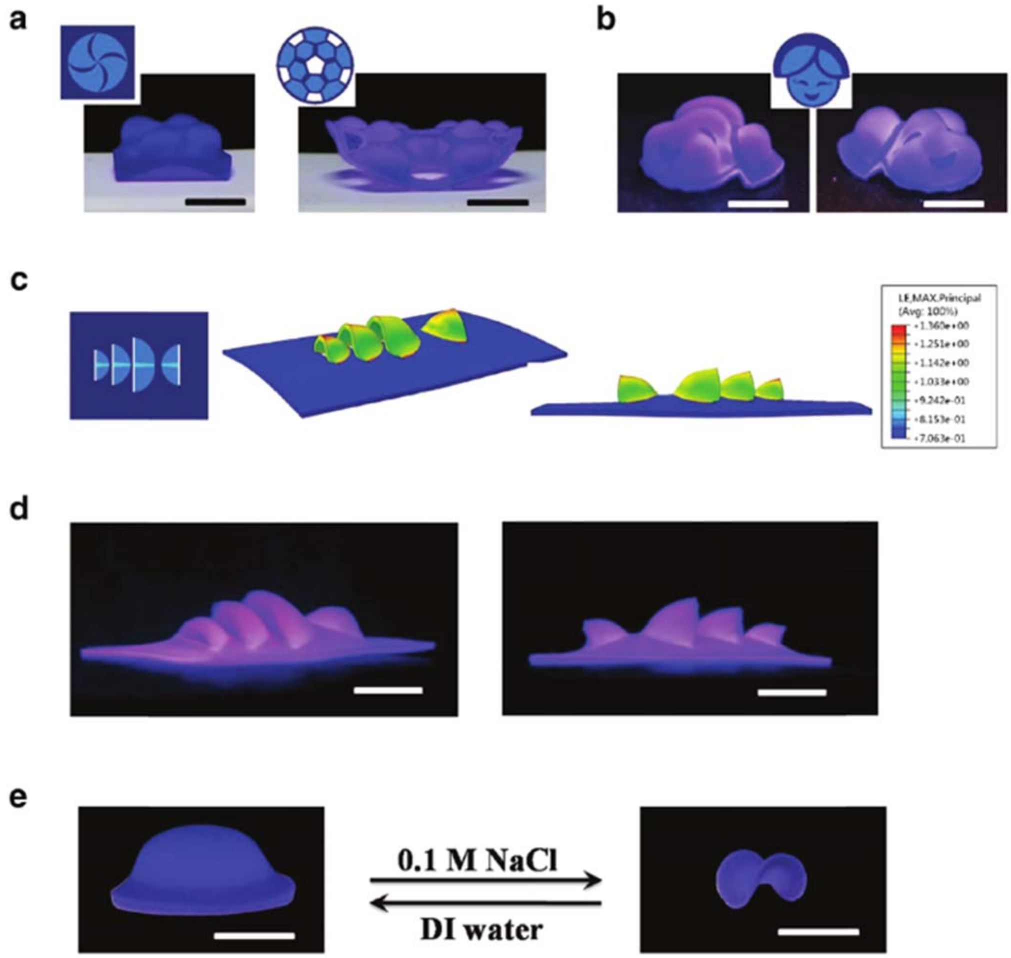

Figure 6. (a) Printed multi-scale buckled structures. (b) 3D cartoon face mask viewed from two different angles. (c) Finite element analysis (FEA) modeling of a 3D theater. From left to right: planar printing layout, 3D theater viewed from two different angles, and the corresponding strain map scale. (d) Photographic images of actual printed 3D theater viewed from two different angles. (e) Printed 4D object, that is, 3D object with active shape changing capability. Reproduced with permission.[66] Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

a dual-function tube capable of simultaneous elongation and gripping that can reach into a tank and grab an object. This approach shows good possibility to be implemented in the soft robotics field by designing complicated assemblies, including those with soft and rigid segments or those with multiple temperature responsive gels.[73,74]

Mulakkal et al. developed a stimuli responsive cellulosic pulp hydrogel composite ink for extrusion-based 3D printing and established its suitability for 4D printing of responsive structures.[75] Montmorillonite clay was added to the ink to enhance storage stability of the composite ink formulations and to improve the extrusion characteristics. They exhibited that the ink could be applied to fabricate complex structure via 3D printing and capable of transforming in response to hydration/dehydration according to pre-determined design (Fig. 10). Another type of composite hydrogels ink consisted of agarose nanofibers, laponite clay and polyacrylamide was utilized by Guo et al. for developing 4D printing hydrogel (4D gel) having high mechanical strength.[76] The formulated 4D Gel showed the ability to transform its shapes. As a proof of concept, they constructed a whalelike hydrogel, which opened mouth and cocked tail by treating with an external force and then cooling, and an octopus like hydrogel with waved tentacles (Fig. 11). The disadvantage of their system is, the material cannot autonomously transform from its original shape but it has to be dependent on an external force.

Along with new materials, researchers are also focusing on customized printing systems in order to fabricate 4D printable complex structure more efficiently. For example, Uchida et al. demonstrated a new fabrication method for 4D printing to construct 3D multi-hydrogels structures with internal gaps.[77] They introduced carboxymethyl cellulose aq (CMC aq)—as a supporting viscous liquid during printing while thermoresponsive poly-N-isopropylacrylamide (pNIPAM) and hydrophilic nonresponsive polyacrylamide (pAAM) pregel solution were used as printing ink. The polymerization of the printed structures was done using ultraviolet (UV) light irradiation. They discussed different parameters for printing and polymerization conditions along with successful demonstration of deformations of the printed structures in response to the temperature. Figure 12 shows variations of 4D structures to demonstrate the effectiveness of their proposal. Although, there are few challenges (flow of the supporting viscous liquid during printing, diffusion of printed ink to supporting ink) to this method, yet the proposed method would be beneficial for printing complex 4D structures with multiple functions that will find useful functions in environmental monitoring and medical applications.

Shinoda and coworkers proposed development of a 4D printer for UV curable gel materials that can simultaneously print out and deform the 3D printed structure.[78] The printing process was similar to that of the conventional 3D-printing process while introduction of a magnetic field during the printing process made their approach unique to the existing printing systems. They applied a magnetic field to set magnetic anisotropy in the curing portion during the building step. This anisotropy is set in each portion of the structure so that the printed structures could deform under an applied

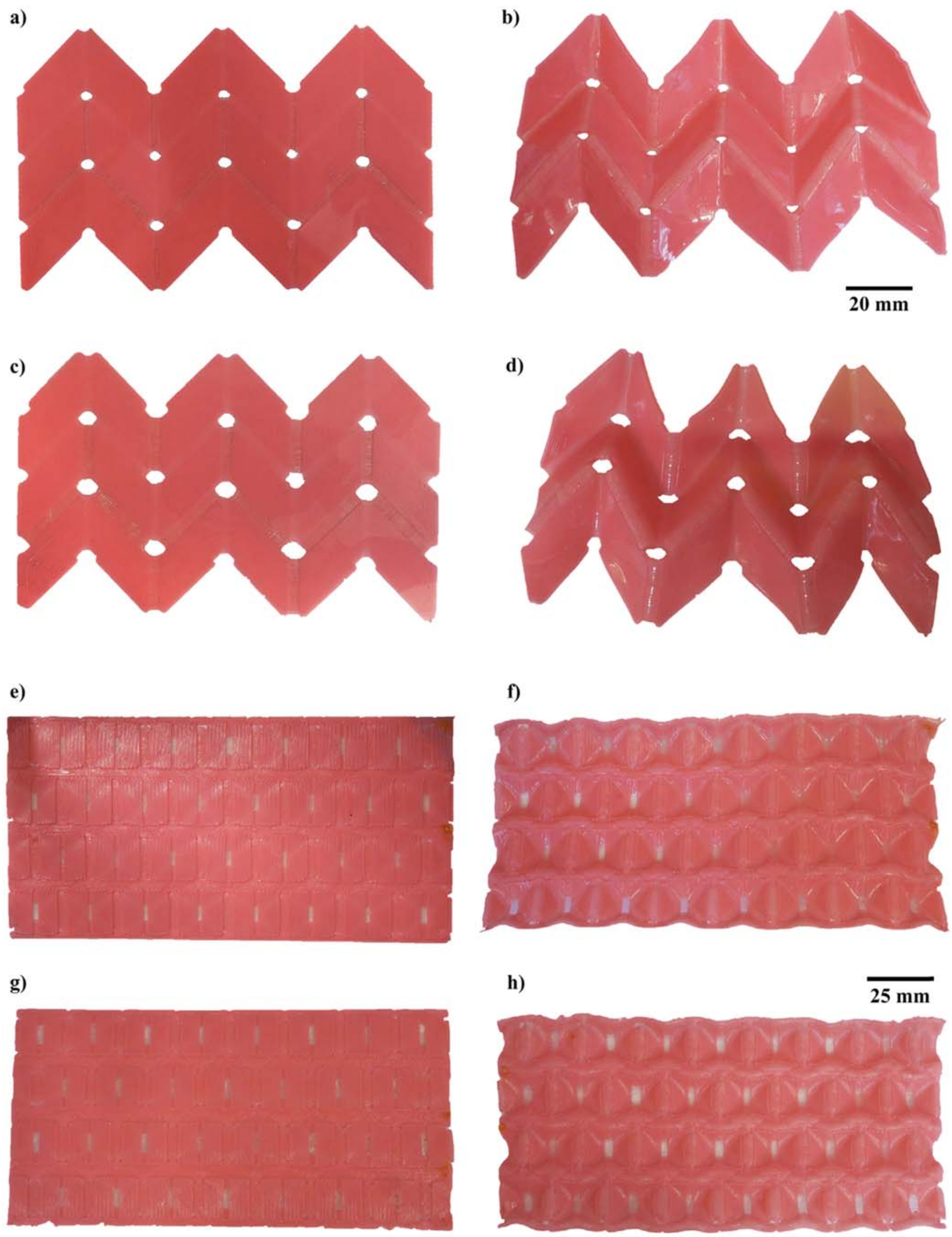

Figure 7. Actuation of Miura-ori origami fold pattern, containing 10 vertices, from dehydrated (left) to hydrated (right); small actuation angles (a) & (b) and large actuation angles (c) & (d). Scale 1:0.59. Actuation of waterbomb origami fold pattern, containing 75 vertices, from dehydrated (left) to hydrated (right); small actuation angles (e) & (f) and large actuation angles (g) & (h). Scale 1:0.47.[70]

magnetic field. Using this technique, they demonstrated a worm-type soft actuator that can crawl in a narrow gap and an array of artificial cilia can reproduce a metachronal wave. They also illustrated a computational method to design the deformation of the structure.

Few works on customized 4D printing techniques that are mainly focused for elastomeric soft materials but have high potential to be applied for gel type materials as well. For instance, Kotikian et al. reported a high-temperature direct ink writing system using liquid crystalline elastomeric inks in order to align the mesogenic domains to the printed actuator.[79] Another very interesting work on customized 3D printing has been recently reported by Skylar-Scott et al. where voxelated soft matter with origami and robotic functions was fabricated using multimaterial multinozzle 3D (MM3D) printing.[80] If such printing systems are applied or improvised for gel materials, their applications and functions will be largely expanded.

Gel-based Bioactive Material Opportunities

Development of smart and highly biocompatible materials for 4D printing is becoming an emerging research area. For the biomedical application, new bioactive material that will change its properties with time and condition are essential to make rapid advancement in this sector. With the expansions in material science, various materials e.g., biopolymers,[81,82] lipids,[83,84] and liquid metals[85] have been made printable. The materials for 4D bioprinting refer to responsive biocompatible materials that are able to reshape or change their function according to external stimuli, including temperature,[38,81,86] water,[83,84] magnetic field,[21] and so on. These stimuli trigger the bio-printed architectures (e.g., scaffolds for tissue engineering), comprising one or multiple materials to reshape and transform into different structures. By utilizing the potential of 3D printing to fabricate tissue-like constructs made of responsive

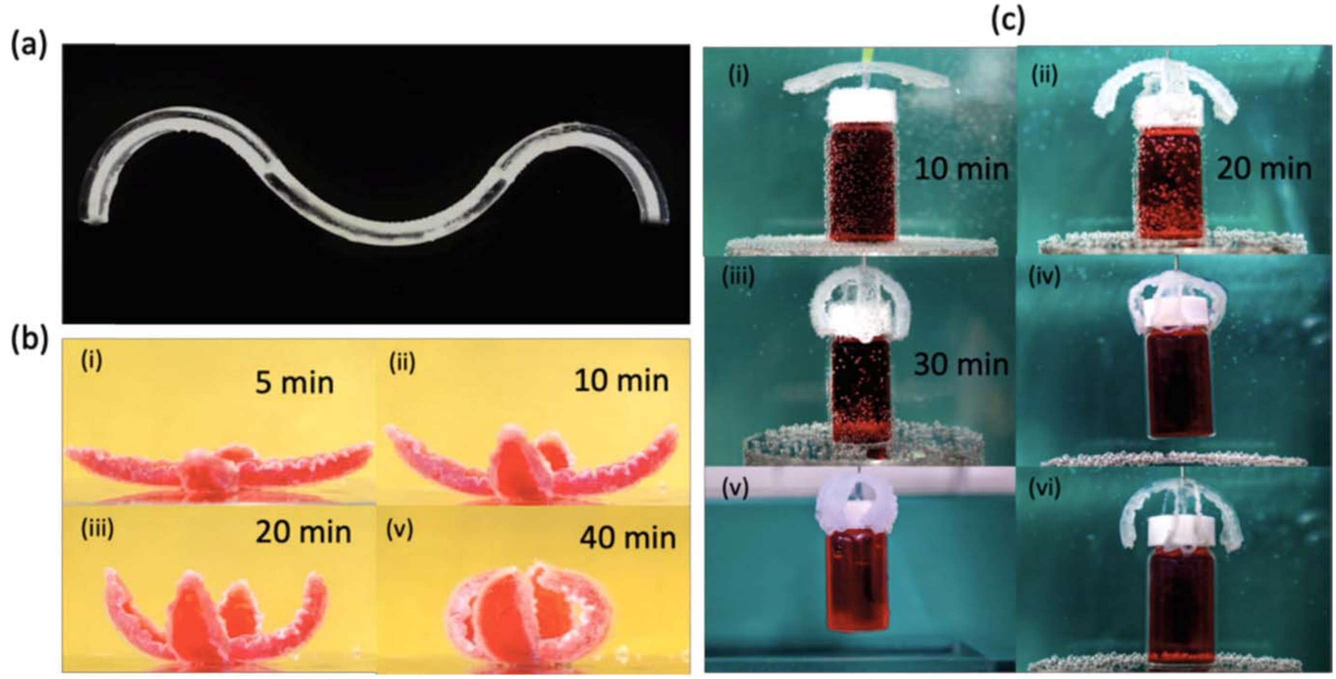

Figure 8. (a) Sinusoidal shape composed of the bilayer alternating at different positions, (b) transformation of the flat flower shape to the 3D blooming state in water (50 °C), and (c) 3D macroscopic gripper at different bending positions (i) before gripping the vial, (ii) before gripping the vial, (iii) in the gripped state, (iv) lifting the vial in water at r.t., (v) lifting the vial in air at r.t., and (vi) releasing the vial in water at 70 °C. Reproduced with permission.[71] Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Reprinted with permission.

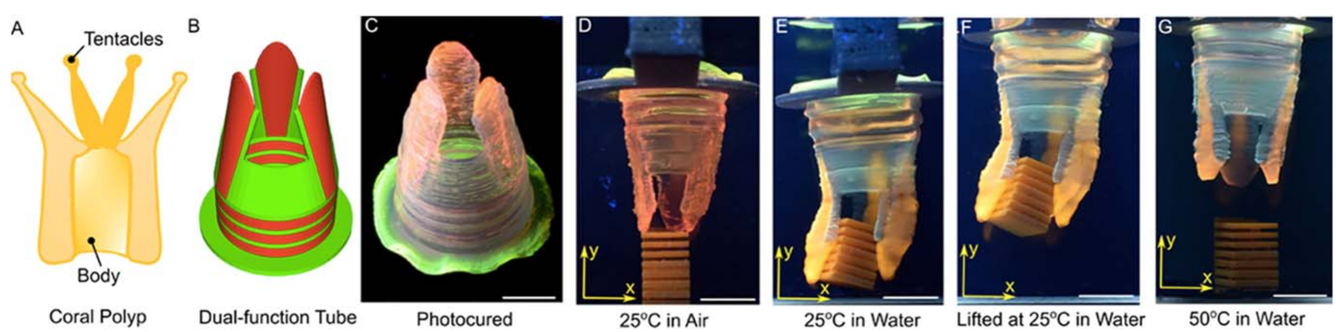

Figure 9. Dual-shape change tubes. (a) Schematic of the basic anatomy of the coral polyp; the image was created based on encyclopedic depictions of the polyp.50 (b), (c) CAD model and image of a 3D-printed and photocured tube with cylindrical base and three fingers. (d)−(g) Optical snapshots of shape change of the tube at different temperatures. The tube was suspended over a part placed in a tank. When water was added to the tank, the tube shows uniaxial elongation and gripping of the part. Upon heating to 50 °C, the tube shortened and the fingers opened to release the part back to the bottom of the tank. Scale bars are 1 cm. Reproduced with permission.[72] Copyright © 2019 American Chemical Society.

materials, it is possible to generate more complex structures similar to native tissues, such as liver[87] and heart.[88] Thus, introducing the fourth dimension "time" will make a significant contribution to the bioprinting of functional tissues or even organs.

For instance, a bilayer printed model using PNIPAAm and water-insoluble polymer poly(e-caprolactone) (PCL) can self-fold or self-unfold in response to temperature, and can be used for yeast cell encapsulation and release.[89] Another thermoresponsive platform comprising poly(acrylic acid)–PNIPAAm and ceramic powder (Al_2O_3) can undergo a tunable sol-gel transition in response to a thermal stimulus.[86] Typically, the procedure involves mixing the thermosensitive polymer with cells, nutrients, or growth factors, and the mixture is then injected into the body. Upon injection, due to the temperature increase, the polymer undergoes a phase transition and forms a gel, releasing its contents from the 3D structure.[90]

Mandon et al. proposed enzymatic reactions by 4D printing and demonstrated two possible approaches for bio sensing and biomimetic application.[91] The first one is based on the printing of the enzymatic couple glucose oxidase/peroxidase for the chemiluminescent detection of glucose, and the second uses printed alkaline phosphatase to generate in situ programmed and localized calcification of the printed object. They demonstrated that the sequential enzymes could retain shape in 3D architecture and worked sequentially to produce light with glucose and high-resolution printing has been attained with alkaline phosphatase–modified 3D ink. These concepts might realize influential implement in tissue engineering.

Mathews et al. designed a bio-nano hybrid ink with optimized compositions of acrylic polymer resin, silver nanoparticles (Ag NP), carbon nanotubes (CNT)[92] and proposed a new fourth dimension i.e. "function" in place of time. The printed materials possess the shape of three-dimensional structures placed together with the bio-functionality of photo electrochemical cells within optimized device flexibility. They showed that the 3D printed structures possess the ability to keep the inherent property of the biomolecule in the structure and simulate its function as in the biological system. They ensured the stability of bacteriorhodopsin (bR) by wrapping with the amphiphilic beta-sheet peptide with an acrylic moiety. The proton

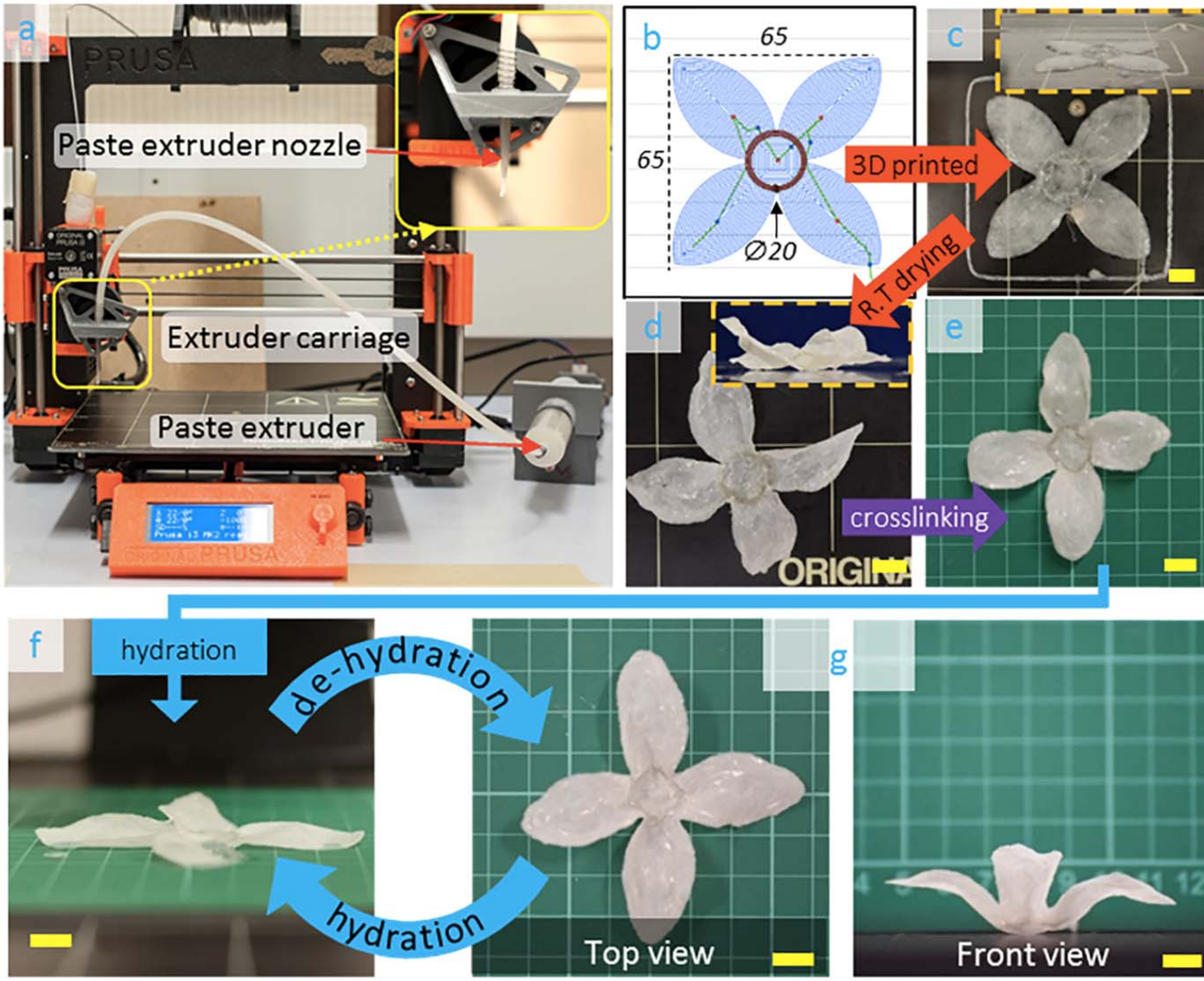

Figure 10. (a) 3D printer and paste extruder set up; Extruder housing is shown in insert with the nozzle for printing gel and composite materials. (b)–(g) Fabrication of petal architecture (b) Generated print path from CAD model—dimensions are in mm (c) 3D printed form (d) Drying at room temperature initiating morphing (e) After crosslinking to maximize and fix the 3D shape (f) Deployed to flat configuration upon hydration (g) drying (dehydration) recovers the 3D petal shape. Side views are shown in insert. (Scale bar = 10 mm).[75]

pump bR is reproduced inside the printed structure and together with the combined effect of silver nanoparticles and carbon nanotubes where the whole system represented as a bio photo reaction. The efficiency of the photo electrochemical has been found to be highly dependent on the thickness of the printed domain. The printed materials with thermo-mechanical properties can be of practical use in development of multifaceted biomaterial.

Kirillova et al. has developed a new method of printing shape-morphing biopolymer hydrogels with living cells.[93] Their approach allows fabrication of hollow self-folding tubes with extraordinary control over their diameters and architectures at high resolution. Two different biopolymers (alginate and hyaluronic acid) and mouse bone marrow stromal cells has been employed for demonstrating the differentiation process. By controlling the printing and post-printing parameters, average internal tube diameters as low as 20 μm has been attained, which is comparable to the diameters of the smallest blood vessels. The 4D bioprinted hydrogel-based tubes can support cell survival for at least 7 days without any decrease in cell viability. Consequently, the proposed 4D bioprinting/biomaterial printing approaches permit the fabrication of dynamically tailorable architectures with tunable functionality and responsiveness with potential application in tissue engineering and medical field.

Challenges in 4D Printing of Gel Materials

4D printing sector is still an emergent field with very limited number of material and methods being capable to show 4D printing features. Thus, this technology is facing some major challenges, for instance limited materials, devices for 3D printing and related software to design or predict the target shape and size. From material engineering point of view only very selective gel materials have been possible to apply in 4D printing. The properties that can be utilized to trigger shape morphing characteristics (e.g. temperature, solvent and pH sensitivity) are also very limited. Besides these, existing self-assembly or self-folding 4D printed structures are predominantly restricted to the size i.e. macroscale deformations are mainly explored, which restricts the precise spatial manipulation of 4D-printed structures. Furthermore, majority of the responsive materials are triggered by only one type of stimulus while tissue engineering purposes, printed 3D scaffolds should adapt to intricate micro surroundings within the living body where multiple signal might be required.[94,95]

Therefore, it is requisite to develop new gel materials that can be capable of tune more easily, for instance magnetic and electroactive gels with good mechanical, electrochemical tunability and fast responsivity should be developed. Every 4D printable material is a

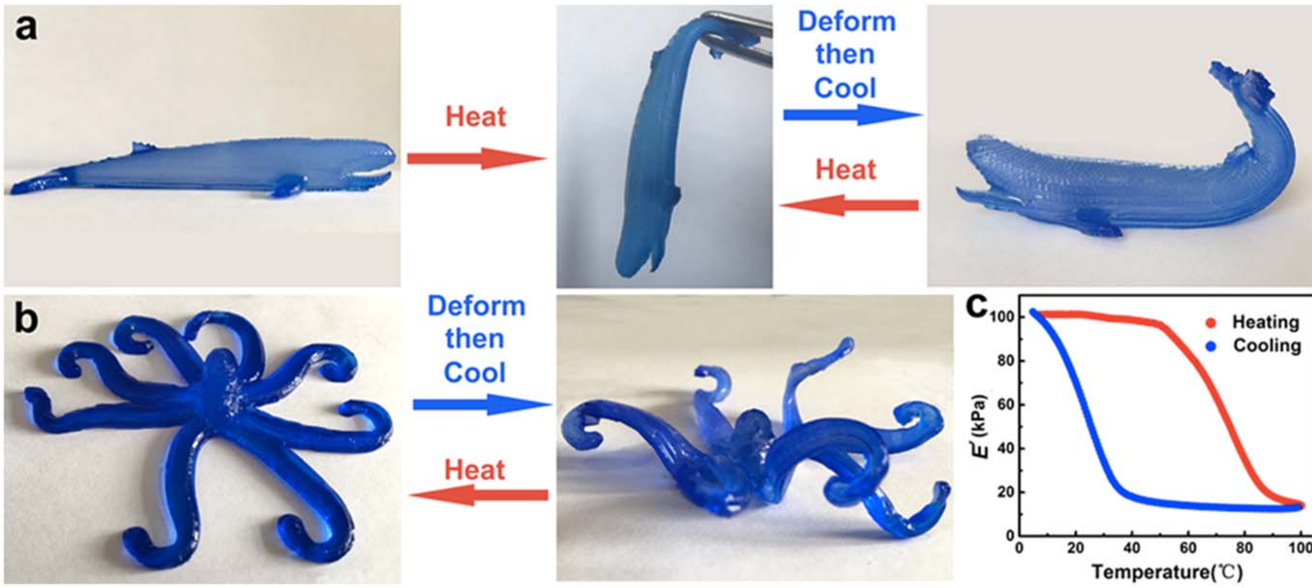

Figure 11. 4D printing product printed by 4D ink: a whale like hydrogel was used as a model to schematic the 4D transition process (a), the softening and hardening cycles of an octopus like gel (b), the storage modulus (E′) variation of 4D Gel during heating and cooling cycles measured by rheology (c). Reproduced with permission.[76] Copyright © 2018 American Chemical Society.

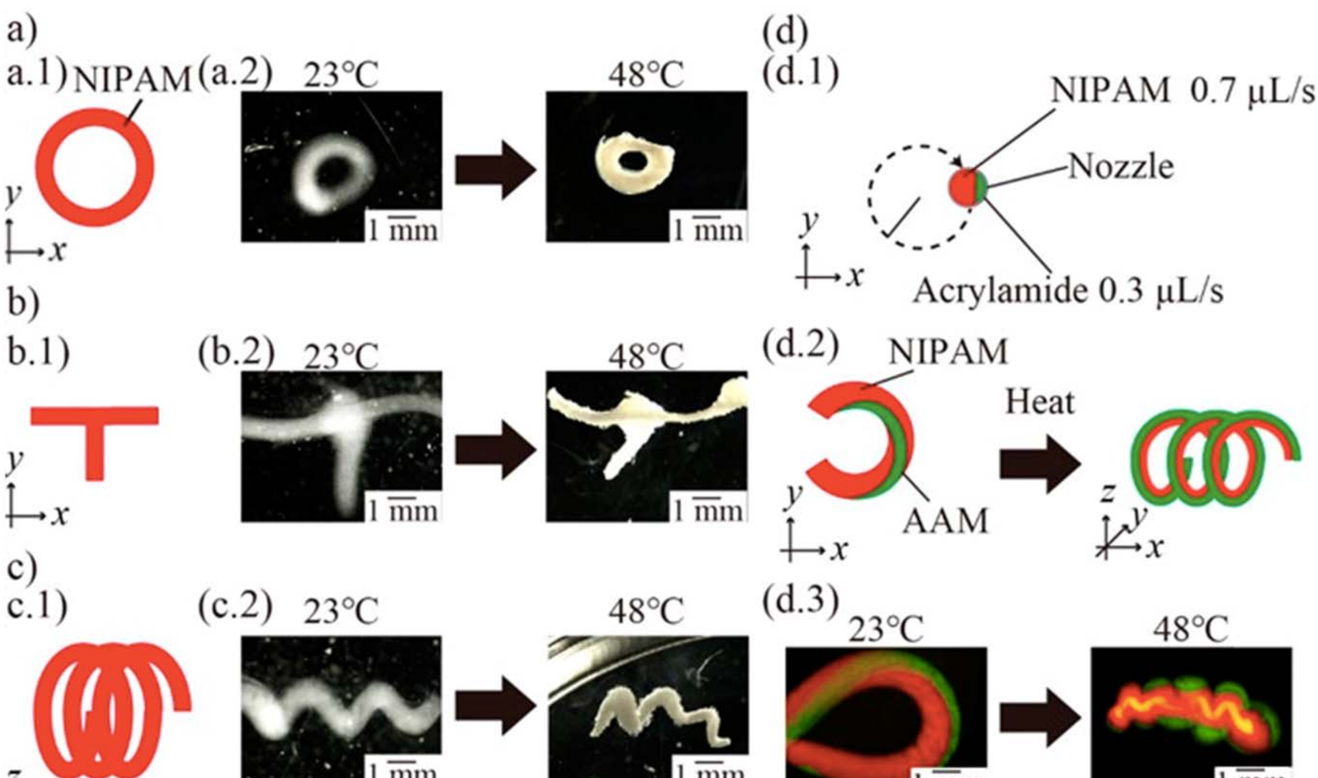

Figure 12. A demonstration of 4D printing. (a) Schematic illustration and images of printed structures and heated structures with a rounded pattern. (b) Schematic illustration and images of a fabricated T-shaped structure and a heated T-shaped structure with a cross point. (c) Schematic illustration and images of a fabricated spring structure and heated spring structure with an internal gap. (d) Schematic illustrations of printing a C-shaped structure with multi-hydrogels (d.1) and its 3D deformation from the C-shaped structure to the spring-shaped structure. (d.2) Fluorescence images of the fabricated C-shaped structure (d.3) and the transformed spring structure obtained by heating. (d.4) Time-lapse images of the C-shaped structure.[77]

kind of stimuli receptor or in other word sensor by which they can sense their surroundings and response according to their characteristic abilities. As a result, they are becoming popular in sensor and robotics field by virtue of their simultaneous sensing and actuation. One of the interesting work in the field of 3D printed sensor is reported by Truby et al.[96] They have developed soft somatosensitive pneumatic actuators (SSAs) incorporating ionic liquid-based gel via embedded 3D printing process that simultaneously enable haptic, proprioceptive, and thermoceptive sensing. This type of work would be more fascinating if the material could be actuated in a contactless way by solely sensing the outer environment. Iongels and composite gels with conductivity or magnetic properties are potential materials to avail noteworthy implementations in the 4D sensing field. The success of 4D printing field also depends on the deeper focus on microscale controllability over the shape, orientation, morphology and biocompatibility of the printed structures.

Designing structures that can transform from one uninformed shape into any distinct shape is another major challenge. This requires major progression in both hardware and software front that can enable actual applications. It is essential to develop complex material programmability, detailed multi-material printing and a variety of highly specific joint designs for folding, curling, twisting, linear expansion/shrinkage etc. On the software side, the challenge requires sophisticated simulation and topology transformation to include the fabrication and material constraints and in the near future, material optimization for efficient structures. Chung et al. addressed the requirement of appropriate 4D printing software to produce effective 4D printing outputs.[97] They discussed the limitations and provided six types of software solutions to fully support corresponding stages in the 4D printing process which are: simulation, modelling, slicing, host/firmware, monitoring, and printing management software, respectively. So far, a few commercial software are being applied to control the shape-changing systems in a well-ordered manner. For examples, Foundry from MIT's Computer Science and Artificial Intelligence Lab,[98] CANVAS software from Mosaic Manufacturing, Project Cyborg from Autodesk[98] and Monolith multi material voxel software are existing tools for self-assemblies simulation and printing parameters optimization.[99] Besides, programming tools like Origamizer and E-Origami System can help to create complex origami shapes through assigning nodes, edges, paths, polygons, vertices, and creases in the structures.[100,101] Also several mathematical models has been employed either to understand to understand the relationship between energy storage and release process during shape memory cycle (spring-mass system), or to illustrate the creep behaviour (four-element model), or to describe polymer chain relaxation process (1D standard linear solid model).[102–104] However, the existing tools are not enough to completely define all types of responsive materials and a continues advancement in these areas, specifically aiming for the applications to 4D printing is becoming the urge of the current age. In addition, easy operation and multitasking functions in both hardware and software fields should be taken into particular consideration.

4D printing also possesses challenges for materials with robust shape-changing capability for a large number of repeatable cycles. Raviv et al. stated that the printed scaffolds could only fully recover to its original shape for a small number of cycles where after repeatedly folding/unfolding the printed objects they experienced severe mechanical degradation due to repeated wetting/drying cycles.[37] To this end, it is imperative to design the mechanics of the stimuli-responsive bioinks/ printed specimens in terms of mechanical engineering perspective especially when repeated responsiveness is desired.

Moreover, complexity in the shape transformation also needs improvement to suit for the increasing demand in 4D bioprinting to construct objects with wide spectrum of applications. For instance, biological tissues usually require multiple foldup to realize full functionality principally for those undergoing development and growth. For bio-robotics field as well repeated but distinctive folding events might be essential to render them preferred efficiencies. To advance the innovation in 4D printing, it is consequently crucial to incorporate rational computer designs of sophisticated multiple stimuli-responsive procedures in order to further boost its widespread implementation in building complex, self-morphing objects in mechanical engineering, soft robotics and bio-engineering field.

Also, the activation process for shape morphing is very limited and mainly dependent on overall heat sensitivity, swelling etc. of the material which is sensed in a bulk category that hinders proper control. More sophisticated method for triggering should be developed where activation of the material can be done in a more controlled and precise way for example by electrical process by resistive or induction heating where heating can be localized precisely and actuation can be done with high accuracy. Another possible way can be, development of printable composite hydrogels with magnetic and electric properties. As mentioned earlier, composite gels are already offering advantageous functionalities over pure hydrogel-based systems.

Last but not the least, to realize 4D structures of gel based smart materials in association with sophisticated and complex design, more versatile 4D printing concepts and devices should be developed, or existing highly functional 3D printers should be upgraded.

Conclusions

4D printing is still in its early stage of research that has created huge potential in the numerous sectors and generated limitless imagination among the researchers. Here we have reviewed the most recent and important advances in the field of 4D printing focusing the potentials of gel-based materials in the field of soft robotics and biomedical engineering. We believe that innovation in the material, fabrication, design and modelling will create further progress in this field. 4D printing in the biomedical field has the potential to physically enable the expansion of biology and bring organ printing one step closer to reality. So, in order to successfully apply 4D printing in practical applications, continuous progress should be made to overcome the current challenges and only then this technology will bring out its best features for the future world.

Acknowledgments

This study has been partly supported by the Grant-in-Aid for Scientific Research (Category A, Project No. 17H01224, etc.) from the Japan Society for the Promotion of Science (JSPS), the Center Of Innovation (COI) program from the Japan Science and Technology Agency (JST), the Strategic Innovation Creation Project (SIP) from the New Energy and Industrial Technology Development Organization (NEDO) of Japan, and the Program on Open Innovation Platform with Enterprises, Research Institute and Academia (OPERA) from the JST.

References

1. D. Pei Eujin, J. Shen, E. Pei, and J. Watling, *Rap. Pro. J*, **21**, 556 (2015).
2. K. Kadimisetty, I. M. Mosa, S. Malla, J. E. Satterwhite-Warden, T. M. Kuhns, R. C. Faria, N. H. Lee, and J. F. Rusling, *Biosens. Bioelectron.*, **77**, 188 (2016).
3. Y. Jiang and Q. Wang, *Sci. Rep.*, **6**, 34147 (2016).
4. M. Vatani, Y. Lu, E. D. Engeberg, and J. W. Choi, *Int. J. Precis. Eng. Manuf.*, **16**, 1375 (2015).
5. M. Stanton, C. Trichet-Paredes, and S. Sanchez, *Lab Chip*, **15**, 1634 (2015).
6. W. G. Yang, H. Lu, W. M. Huang, H. J. Qi, X. L. Wu, and K. Y. Sun, *Polymers*, **6**, 2287 (2014).
7. T. A. Campbell, S. Tibbits, and B Garrett, *Atlantic Council*, 1 (2014).
8. T. A. Campbell and O. S. Ivanova, *Nano Today*, **8**, 119 (2013).
9. M. N. I. Shiblee, K. Ahmed, A. Khosla, M. Kawakami, and H. Furukawa, *Soft Matter*, **14**, 7809 (2018).
10. K. Ahmed, N. Naga, M. Kawakami, and H. Furukawa, *Macromol. Chem. Phys.*, **1800216**, (2018).
11. K. Ahmed, M. Kawakami, A. Khosla, and H. Furukawa, *Polym. J.*, **51**, 511 (2019).
12. F. Cock, A. Cuadri, M. García-Morales, and P. Partal, *Polym. Test.*, **32**, 716 (2013).
13. O. Ivanova, A. Elliott, T. Campbell, and C. Williams, *Add. Man.*, **1**, 24 (2014).
14. X. Liu, Y. Zheng, S. R. Peurifoy, E. A. Kothari, and A. B. Braunschweig, *Polym. Chem.*, **7**, 3229 (2016).
15. Z. Quan, A. Wu, M. Keefe, X. Qin, J. Yu, J. Suhr, J. H. Byun, B. S. Kim, and T. W. Chou, *Mat. Today*, **18**, 503 (2015).
16. A. Zolfagharian, A. Z. Kouzani, S. Y. Khoo, A. A. A. Moghadam, I. Gibson, and A. Kaynak, *Sens. Actuators, A*, **250**, 258 (2016).
17. E. Pei, *Assembly Autom*, **34**, 310 (2014).
18. J. A. Lewis, *Adv. Funct. Mater.*, **16**, 2193 (2006).
19. S. Tibbits, *Archit Des*, **84**, 116 (2014).
20. K. Sun, T. S. Wei, B. Y. Ahn, J. Y. Seo, S. J. Dillon, and J. A. Lewis, *Adv. Mater.*, **25**, 4539 (2013).
21. D. Kokkinis, M. Schaffner, and A. R. Studart, *Nat. Commun.*, **6**, 8643 (2015).
22. J. O. Hardin, T. J. Ober, A. D. Valentine, and J. A. Lewis, *Adv. Mater.*, **27**, 3278 (2015).
23. S. M. Felton, M. T. Tolley, B. Shin, C. D. Onal, E. D. Demaine, D. Rus, and R. J. Wood, *Soft Matter*, **9**, 7688 (2013).

24. K. Otsuka and C. M. Wayman, in *Shape Memory Materials* (Cambridge Univ. press, Urbana-Champaign) (1998).
25. J. M. Jani, M. Leary, A. Subic, and M. A. Gibson, *Mater. Desig*, **56**, 1078 (2014).
26. G. G. Wallce, P. R. Teasdale, G. M. Spinks, and L. Kane-Maguire, in *Conductive Electroactive Polymers: Intelligent Polymer Systems* (CRC Press, USA) (2008).
27. B. F. Coulter and A. Ianakiev, *3d Printing and Additive Manufacturing*, **2**, 140 (2015).
28. M. Cianchetti, R. Tommaso, G. Giada, N. Thrishanta, A. Kaspar, D. Prokar, and M. Arianna, *Soft Robo*, **1**, 122 (2014).
29. J. Ryu, M. D'Amato, X. Cui, K. N. Long, H. J. Qi, and M. L. Dunn, *Appl. Phys. Lett.*, **100** (2012).
30. S. A. M. Tofail, E. P. Koumoulos, A. Bandyopadhyay, S. Bose, L. O'Donoghue, and C. Charitidis, *Mat. Tod.*, **21**, 22 (2018).
31. S. F. S. Shirazi, S. Gharehkhani, M. Mehrali, H. Yarmand, H. S. C. Metselaar, N. A. Kadri, and N. A. A. Osman, *Sci. Technol. Adv. Mater.*, **16**, 033502 (2015).
32. K. F. Leong, K. K. Phua, C. K. Chua, Z. H. Du, and K. O. Teo, *Proc. Inst. Mech. Eng.*, **215**, 191 (2001).
33. Z. Zhao, J. Wu, X. Mu, H. Chen, H. J. Qi, and D. Fang, *Macromol. Rapid Commun.*, **38**, 201600625 (2017).
34. E. Pei, *Assem. Auto.*, **34**, 310 (2014).
35. S. Tibbits, http://ted.com/talks/skylar_tibbits_the_emergence_of_4d_printing (2013).
36. T. Campbell, S. Tibbits, and B. Garrett, *Frame*, (2014).
37. D. Raviv et al., *Sci. Rep.*, **4**, 07422 (2014).
38. S. E. Bakarich, R. Gorkin, and G. M. Spinks, *Macro. Rap. Comm.*, **36**, 12,1211 (2015).
39. T. Xie, *Nature*, **464**, 267 (2010).
40. Q. Zhao, H. J. Qi, and T. Xie, *Polym. Sci.*, **49**, 79 (2015).
41. Q. Zhao, W. Zou, Y. Luo, and T. Xie, *Sci. Adv.*, **2**, 1501297 (2016).
42. M. Zheng, Z. Fang, W. Zou, Q. Zhao, and T. Xie, *Chem. Int. Ed.*, **55**, 11421 (2016).
43. V. D. L. Hj, S. Herber, W. Olthuis, and P. Bergveld, *Analyst*, **128**, 325 (2003).
44. M. Prabaharan and J. F. Mano, *Macromol. Biosci.*, **6**, 991 (2006).
45. I. Tokarev and S. Minko, *Soft Matter*, **5**, 511 (2009).
46. Y. Qiu and K. Park, *Adv. Drug. Deliv. Rev.*, **64**, 49 (2012).
47. R. Shankar, T. K. Ghosh, and R. J. Spontak, *Soft Matter*, **3**, 1116 (2007).
48. Z. Yang, G. A. Herd, S. M. Clarke, A. R. Tajbakhsh, E. M. Terentjev, and W. T. Huck, *J. Am. Chem. Soc.*, **128**, 1074 (2006).
49. M. Bodaghi, A. R. Damanpack, and W. H. Liao, *Mater. Des.*, **135**, 26 (2017).
50. C. Yang, M. Boorugu, A. Dopp, J. Ren, R. Martin, D. Han, W. Choi, and H. Lee, *Mater. Horiz.*, **6**, 1244 (2019).
51. C. Löwenberg, M. Balk, C. Wischke, M. Behl, and A. Lendlein, *Acc. Chem. Res.*, **50**, 723 (2017).
52. A. Ghosh, C. Yoon, F. Ongaro, S. Scheggi, F. M. Selaru, S. Misra, and D. H. Gracias, *Front. Mech. Eng.*, **3**, 7 (2017).
53. J. C. Breger, C. K. Yoon, R. Xiao, H. R. Kwag, M. O. Wang, J. P. Fisher, T. D. Nguyen, and D. H. Gracias, *ACS Appl. Mater. Interfaces*, **7**, 3398 (2015).
54. C. Yoon, R. Xiao, J. Park, J. Cha, T. D. Nguyen, and D. H. Gracias, *Smart Mater. Struct.*, **23**, 094008 (2014).
55. S. Nakajima, R. Kawano, and H. Onoe, *Soft Matter*, **13**, 3710 (2017).
56. C. Ma, W. Lu, X. Yang, J. He, X. Le, L. Wang, J. Zhang, M. J. Serpe, Y. Huang, and T. Chen, *Adv. Funct. Mater.*, **28**, 1 (2018).
57. Z. B. Hu, X. M. Zhang, and Y. Li, *Science*, **269**, 525 (1995).
58. Y. S. Kim, M. Liu, Y. Ishida, Y. Ebina, M. Osada, T. Sasaki, T. Hikima, M. Takata, and T. Aida, *Nat. Mater.*, **14**, 1002 (2015).
59. J. Zheng, P. Xiao, X. Le, W. Lu, P. Théato, C. Ma, B. Du, J. Zhang, Y. Huang, and T. Chen, *J. Mater. Chem. C*, **6**, 1320 (2018).
60. A. S. Gladman, E. A. Matsumoto, R. G. Nuzzo, L. Mahadevan, and J. A. Lewis, *Nat. Mater.*, **15**, 413 (2016).
61. S. Tibbits, C. McKnelly, C. Olguin, D. Dikovsky, and S. Hirsch, *34th Ann. Conf. of the Asso. for Comp. Aided Des. in Architecture* 539 (2014).
62. S. Naficy, R. Gately, R. Gorkin, H. Xin, and G. M. Spinks, *Macromol. Mater. Eng.*, **302**, 1600212 (2017).
63. R. Fernandes and D. H. Gracias, *Adv. Drug Del. Rev.*, **64**, 1579 (2012).
64. B. G. Compton and J. A. Lewis, *Adv. Mater.*, **26**, 5930 (2014).
65. M. D. Dickey, *Nat. Mater.*, **15**, 379 (2016).
66. L. Huang, R. Jiang, J. Wu, J. Song, H. Bai, B. Li, Q. Zhao, and T. Xie, *Adv. Mater.*, **29**, 1605390 (2017).
67. A. Azam, K. E. Laflin, M. Jamal, R. Fernandes, and D. H. Gracias, *Biomed. Microdev.*, **13**, 51 (2011).
68. A. Lendlein and L. Ionov, *Macro. Chem. and Phys.*, **214**, 1178 (2013).
69. Y. Mao, Z. Ding, C. Yuan, S. Ai, M. Isakov, J. Wu, T. Wang, M. L. Dunn, and H. J. Qi, *Sci. Rep.*, **6**, 24761 (2016).
70. A. B. Baker, S. R. G. Bates, T. M. Llewellyn-Jones, L. P. B. Valori, M. P. M. Dicker, and R. S. Trask, *Mater. Design*, **163**, 107544 (2019).
71. M. N. I. Shiblee, K. Ahmed, M. Kawakami, and H. Furukawa, *Adv. Mater. Technol.*, **4**, 1900071 (2019).
72. J. Liu et al., *ACS Appl. Mater. Interfaces*, **11**, 8492 (2019).
73. J. Guo, T. Shroff, C. Yoon, J. Liu, J. C. Breger, D. H. Gracias, and T. D. Nguyen, *Extreme Mech. Lett.*, **16**, 6 (2017).
74. K. Kobayashi, S. H. Oh, C. Yoon, and D. H. Gracias, *Macromol. Rapid Commun.*, **39**, 1700692 (2018).
75. M. C. Mulakkal, R. S. Trask, V. P. Ting, and A. M. Seddon, *Mater. Design*, **160**, 108 (2018).
76. J. Guo, R. Zhang, and L. Zhang, *ACS Macro Lett.*, **7**, 442 (2018).
77. T. Uchida and H. Onoe, *Micromachines*, **10**, 433 (2019).
78. H. Shinoda, S. Azukizawa, K. Maeda, and F. Tsumori, *J. Electrochem. Soc.*, **166**, B3235 (2019).
79. N. A. Peppas, P. Bures, W. Leobandung, and H. Ichikawa, *J. Pharm. Biopharm.*, **50**, 27 (2000).
80. A. Kotikian, R. L. Truby, J. W. Boley, T. J. White, and J. A. Lewis, *Adv. Mater.*, **30**, 1706164 (2018).
81. M. A. Skylar-Scott, J. Mueller, C. W. Visser, and J. A. Lewis, *Nature*, **575**, 330 (2019).
82. M. Jamal, S. S. Kadam, R. Xiao, F. Jivan, T. M. Onn, R. Fernandes, T. D. Nguyen, and D. H. Gracias, *Adv. Healthcare Mater.*, **2**, 1142 (2013).
83. G. Villar, A. J. Heron, and H. Baeley, *Nat. Nanotechnol.*, **6**, 803 (2011).
84. G. Villar, A. D. Graham, and H. Baeley, *Science*, **340**, 48 (2013).
85. Y. Yu, J. Zang, and J. Liu, *PLoS One*, **8**, e58771 (2013).
86. X. Wang, Y. Sun, C. Peng, H. Luo, R. Wang, and D. Zhang, *ACS Appl. Mater. Interf.*, **7**, 26131 (2015).
87. T. Ikegami and Y. Maehara, *Nat. Rev. Gastro Hepat.*, **10**, 697 (2013).
88. S. Weber, R. Sodian, M. Markert, B. Reichart, S. Daebritz, and T. C. Lueth, *Int. J. Comput. Assist. Radiol. Surg.*, **2**, 160 (2007).
89. G. Stoychev, N. Puretskiy, and L. Ionov, *Soft Matter*, **7**, 3277 (2011).
90. A. Gandhi, A. Paul, S. O. Sen, and K. K. Sen, *Asian J. Pharm. Sci.*, **10**, 99 (2015).
91. C. A. Mandon, L. J. Blum, and C. A. Marquette, *Micromachines*, **8**, 102 (2017).
92. A. S. Mathews, S. Abraham, K. S. Kumaran, J. Fanbc, and C. Montemagno, *RSC Adv.*, **7**, 41429 (2017).
93. A. Kirillova, R. Maxson, G. Stoychev, C. T. Gomillion, and L. Ionov, *Adv. Mater.*, **29**, 1703443 (2017).
94. B. Gao, Q. Yang, X. Zhao, G. Jin, Y. Ma, and F. Xu, *Trends Biotechnol.*, **34**, 746 (2016).
95. Z. X. Khoo, J. E. M. Teoh, Y. Liu, C. K. Chua, S. Yang, and J. An, *Virtual Phys Prototyp.*, **10**, 103 (2015).
96. R. L. Truby, M. Wehner, A. K. Grosskopf, D. M. Vogt, S. G. M. Uzel, R. J. Wood, and J. A. Lewis, *Adv. Mater.* (Wiley, USA) **30**, 1706383 (2018).
97. S. Chung, S. E. Song, and Y. T. Cho, *Int. J. of Precis. Eng. and Manuf.-Green Tech.*, **4**, 359 (2017).
98. E. Pei, *Assembly Autom.*, **34**, 123 (2014).
99. D. Gurung, *Technological Comparison of 3D and 4D Printing: Analytical Study* (2017).
100. E. A. Peraza-Hernandez, D. J. Hartl, R. J. Malak Jr, and D. C. Lagoudas, *Smart Mater. Struct.*, **23**, 094001 (2014).
101. J. Mitani, *Comput.-Aided Des. Appl.*, **6**, 69 (2009).
102. H. Tobushi, T. Hashimoto, S. Hayashi, and E. Yamada, *J. Intell. Mater. Syst. Struct.*, **8**, 711 (1997).
103. J. Leng and S. Du, in *Shape-Memory Polymers and Multifunctional Composites* (CRC Press, USA) (2010).
104. X. Hu, J. Zhou, M. Vatankhah-Varnosfaderani, W. F. Daniel, Q. Li, A. P. Zhushma, A. V. Dobrynin, and S. S. Sheiko, *Nat. Commun.*, **7**, 12919 (2016).