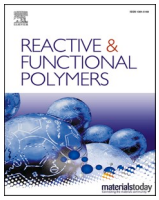
Reactive and Functional Polymers 179 (2022) 105374

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react



Review

4D bioprinting of smart polymers for biomedical applications: recent progress, challenges, and future perspectives

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ARTICLE INFO

Keywords:
4D printing
Shape memory polymers
Hydrogels
Biomedical applications
Scaffolds
Tissue engineering

ABSTRACT

4D bioprinting is the next-generation additive manufacturing-based fabrication platform employed to construct intricate, adaptive, and dynamic soft and hard tissue structures as well as biomedical devices. It is achieved by using stimuli-responsive materials, especially shape memory polymers (SMPs) and hydrogels, which possess desirable biomechanical characteristics. In the last few years, numerous efforts have been made by 4D printing community to develop novel stimuli-responsive polymeric materials by considering their biomedical perspective. This review presents an up-to-date overview of 4D bioprinting technology incorporating bioprinting materials, functionalities of biomaterials as well as the focused approach towards different tissue engineering and regenerative medicine (TERM) applications. It includes bone, cardiac, neural, cartilage, drug delivery systems, and other high-value biomedical devices. This review also addresses current limitations and challenges in 4D bioprinting technology to provide a basis for foreseeable advancements for TERM applications that could be helpful for their successful utilization in clinical settings.

Abbreviations: 3D, Three-dimensional; 4D, Four-dimensional; AESO, Acrylated epoxidized soybean oil; AM, Additive manufacturing; Alg, Alginate; ALP, Allopurinol; AuNRs, Gold nanorods; BCP, Bioengineered cardiac patch; BMA, Benzyl methacrylate; BM-MSCs, Human bone marrow derived mesenchymal stem cells; BPNSs, Black phosphorus nanosheets; BSA, Bovine serum albumin; BTE, Bone tissue engineering; CAD, Computer-aided design; CMCS, Carboxymethyl chitosan; CNTs, Carbon nanotubes; CT, Computed tomography; CTE, Cartilage tissue engineering; CS, Chitosan; DDSs, Drug delivery systems; DIW, Direct ink writing; DLP, Digital light processing; DPEPA, Dipentaerythritol pentaacrylate; EBP, Elastin-based polypeptides; ECM, Extracellular Matrix; FDM, Fused deposition modeling; FEM, Finite element method; Gel, Gelatin; GelMA, Methacrylated gelatin; GLY, Glycerol; GO, Graphene oxide; GO_x, Glucose oxidase; HA, Hyaluronic acid; HAP, Hydroxyapatite; hECs, Human endothelial cells; hiPSC-CMs, Human-induced pluripotent stem cell–derived cardiomyocytes; hMSCs, Human mesenchymal stem cells; HPCT, Hydroxypropyl chitin; IPNs, Interpenetrating polymer networks; IJP, Inkjet printing; LAAO, Left atrial appendage occlude; MA, Methacrylated alginate; MBG, Mesoporous bioactive glass; MCC, Microcrystalline cellulose; MWCNT, Multi-walled carbon nanotube; NAG, N-acetylglucosamine; NIR, Near-infrared radiation; NSCs, Neural stems cells; MRF, Magnetorheological fluid; MHTs, Micro-scaled hollow tubules; MI, Myocardial infarction; MNCs, Magnetic nanocomposites; MNPs, Magnetic nanoparticles; MRI, Magnetic resonance imaging; MSCs, Mesenchymal stem cells; MX-HF, MXene-incorporated hollow fibrous; NPs, Nanoparticles; NTE, Neural tissue engineering; PAA, Poly(acrylic acid); PAEK, Poly(aryl ether ketone); PASP, Poly(aspartic acid); PBS, Poly(butylene succinate); PCL, Poly(ε-caprolactone); PCL-T, Poly(caprolatone) triol; PCLDA, Poly(ε-caprolactone)-diacrylates; PCLMA, Poly(caprolactone) methacrylate; PDA, Polydopamine; PDLLA, Poly(d,l-Lactic Acid); PDMAEMA, Poly(2-dimethylaminoethyl methacrylate); PDMS, Poly(dimethylsiloxane); PEGDMA, Poly(ethylene glycol)-dimethacrylate; PEG, Poly (ethylene glycol); PEGDA, Polyethylene glycol diacrylate; PGDA, Poly(glycerol dodecanoate) acrylate; PGS, Poly(glycerol sebacate); PI, Photo-initiator; PHBV, Poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate); PHDI, Poly(hexamethylene diisocyanate); PHIS, Poly(histidine); PNIPAM, Poly(N-isopropyl acrylamide); PNIPAM-AAc, Poly(N-isopropyl acrylamide-*co*-acrylic acid); PNVCL, Poly(N-vinylcaprolactam); PLA, Poly(lactic acid); PLA-TMC, Poly (lactic acid-*co*-trimethylene carbonate); PLGA, Poly(lactic-*co*-glycolic acid); PLMC, Poly(D,L-lactide-*co*-trimethylene carbonate); PPC, Poly(propylene carbonate); PPF, Poly(propylene fumarate); PtNP, Platinum nanoparticle; PTMC, Poly(trimethylene carbonate); PTT, Photothermal therapy; PTU, Polythiourethane; PU, Polyurethane; PVA, Poly(vinyl alcohol); RQ, Research question; RS, Regenerated silk; SA, Sodium alginate; SLA, Stereolithography; SLM, Selective laser melting; SCMs, Shape changing materials; SMs, Smart materials; SMAs, Shape memory alloys; SMPs, Shape memory polymers; SMPCs, Shape memory polymer composites; SMMs, Shape memory materials; SMMF, Shape-morphing microfish; SMMRs, Shape-morphing microrobots; SLS, Selective laser sintering; SWOT, Strength, weakness, opportunities, and threats; TCP, Tricalcium phosphate; TE, Tissue engineering; TERM, Tissue engineering and regenerative medicine; TGFβ-3, Transforming growth factor beta-3; TSME, Triple shape memory effect; TRL, Technology readiness level; UV, Ultraviolet; βCD, β-cyclodextrin.

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https://doi.org/10.1016/j.reactfunctpolym.2022.105374
Received 24 May 2022; Received in revised form 22 July 2022; Accepted 5 August 2022
Available online 10 August 2022

Table 1
A brief overview of 4D printing technologies applied for TERM and other biomedical applications.

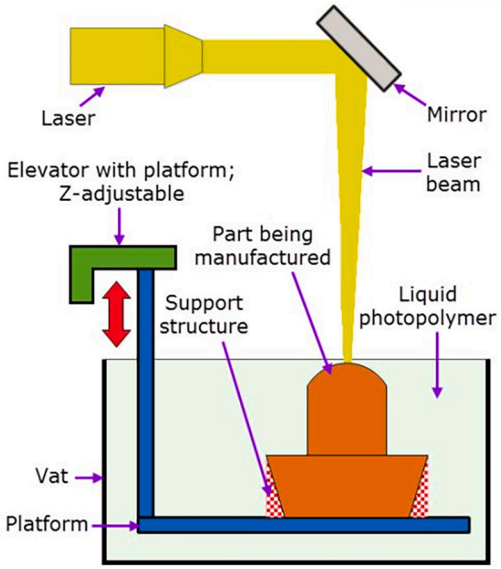
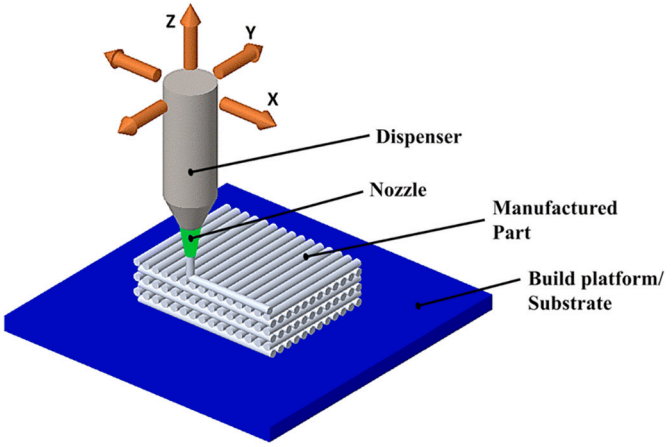
Feedback type	4D bioprinting	Resolution (μm)	Materials	Schematic illustration of processes	Advantages	Disadvantages	Ref
Liquid-based	SLA	50–100	Photo-curable resins and SMPs	 (Adapted from ref. [41] Copyright 2017 Swinburne University of Technology Hawthorn, Victoria, Australia)	**1.** Fabricated products exhibit smooth and excellent surface **2.** Highly accurate technique used to develop intricate structures **3.** Trapped material can be easily removed **4.** Moderate conditions are useful for the loading of cells and biomolecules	**1.** Low tensile properties **2.** Defective decomposition of photo-responsive materials and biocompatibility. **3.** Uncured photo-initiator produce cytotoxicity **4.** Requires highly intense UV radiation to cross-link **5.** Multiple materials layers can't be printed.	[42–44]
	DIW	100–600	Biopolymers, hydrogels	 (Adapted with permission from ref. [45] Copyright 2019, Springer Nature Switzerland AG)	**1.** Develop multi-material architectures **2.** Fabricate porous scaffolds **3.** Use self-supporting filaments **4.** Use thixotropic fluid	**1.** Low printing resolution and reproducibility **2.** Require post-processing	[46–48]
	DLP	10–50	Photo-curable resins, SMPs		**1.** High printing speed **2.** High resolution **3.** Highly compatible with cells	**1.** Low mechanical strength **2.** Less viscous materials **3.** Processing time is long	[50–52]

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Table 1 (*continued*)

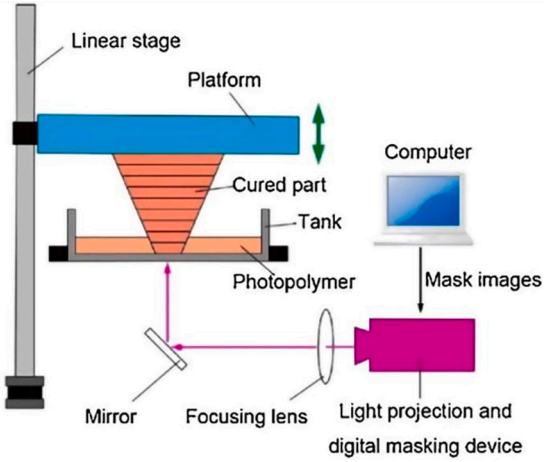
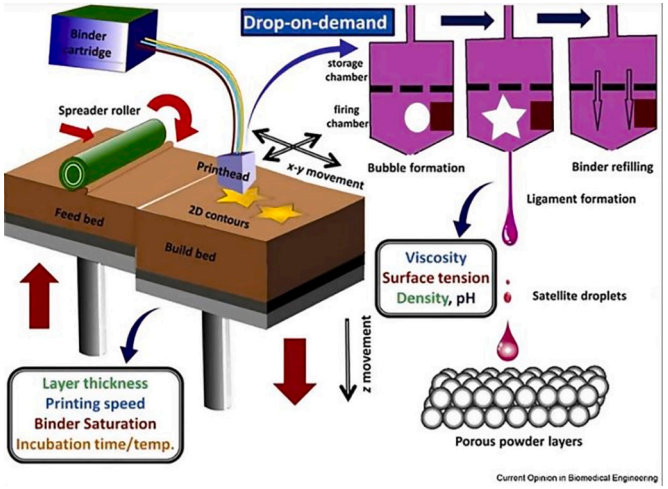
Feedback type	4D bioprinting	Resolution (μm)	Materials	Schematic illustration of processes	Advantages	Disadvantages	Ref
				 (Adapted with permission from ref. [49] Copyright 2018 Elsevier B.V.)			
	IJP	50–300	Hydrogels, SMPs	 (Adapted with permission from ref. [53] Copyright 2017 Elsevier Inc.)	**1.** High compatibility with low-viscous bioactive materials **2.** Ability to Process bio-ink materials incorporating living cells. **3.** Non-contact nozzle	**1.** Difficult to develop intricate products. **2.** Reduced cell viability **3.** Printing of small number of materials due to low viscosity constraint **4.** Low dimensional accuracy	[54–56]
Solid-based	FDM	100–150	SMPCs, polymer composites		**1.** Didn't require support structure **2.** Develop variety of biocompatible materials **3.** Develop tissues by processing high-density cells **4.** Develop porous scaffolds	**1.** Low dimensional accuracy **2.** Slow printing speed **3.** Require high temperature **4.** Low cell viability	[58–60]

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Table 1 (*continued*)

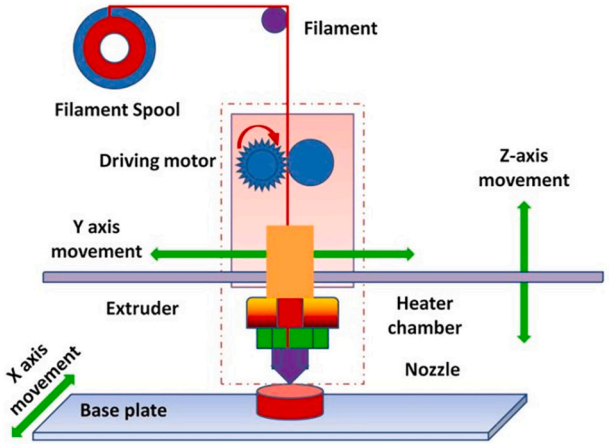
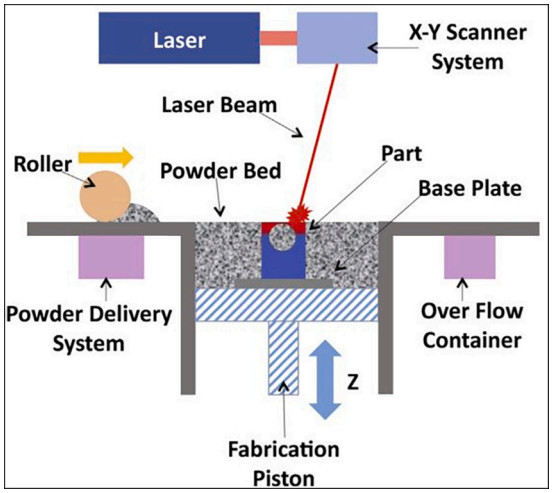
Feedback type	4D bioprinting	Resolution (μm)	Materials	Schematic illustration of processes	Advantages	Disadvantages	Ref
				 (Adapted with permission from ref. [57] Copyright 2022 the Society of Manufacturing Engineers, Elsevier Ltd.)			
Powder-based	SLM	20–100	Synthetic polymers, metals, super alloys	 (Adapted with permission from ref. [61] Copyright 2015 Elsevier B.V.)	**1.** Better surface quality **2.** Excellent biomechanical performance	**1.** Second phase development	[62–64]
	SLS	50–100	Polymers, metals, ceramics		**1.** Didn't require support structure **2.** Develop porous scaffolds	**1.** High temperature **2.** Resolution is dependent on laser beam diameter **3.** High porosity	[66–68]

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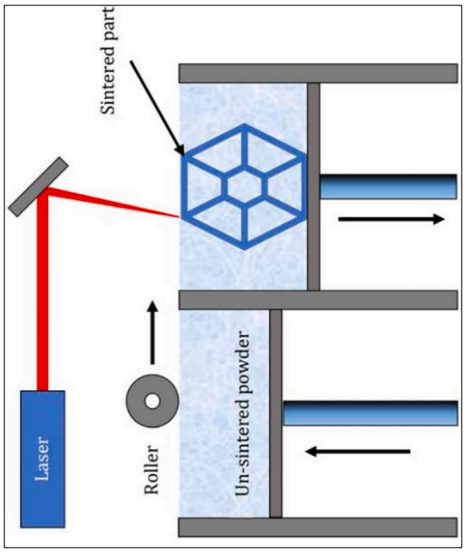
Table 1 (*continued*)

Feedback type	4D bioprinting	Resolution (μm)	Materials	Schematic illustration of processes	Advantages	Disadvantages	Ref
				 (Adapted with permission from ref. [65] Copyright 2015 Academy of Dental Materials, Elsevier Ltd.)		

1. Introduction

Three-dimensional (3D) printing is an emerging additive manufacturing (AM) technology that has been employed in different clinical settings, including organ and tissue fabrication, drug delivery devices, and regenerative medicine [1–4]. The technology applies combining imaging approaches including computed tomography (CT) and magnetic resonance imaging (MRI) to obtain human-specific data which is transformed into computer-aided design (CAD) models and 3D-printed products are constructed [5–8]. This technology has drawn immense attention, as it helps by providing customized biomedical services by 3D printing patient-specific biomedical equipment, as per requirements [9–11]. 3D-printed products mimic excellent physiological properties, however, biomedical devices manufactured through this technology are static in nature and are not designed for the dynamic situations [12–14]. The micro-environment of native tissues in the living body supports their development as well as modulates their biological functions [15–18]. For better performance, the bioactive materials should be adaptable to the dynamic environment along with their excellent biodegradability and biocompatibility requirements [19–22]. Four-dimensional (4D) printing technology has been developed to counter this problem. In 2013, the idea of 4D printing was first provided by Prof. Tibbits and Prof. Jerry, in which advanced materials morph their shape with respect to time in a simulated environment [23–25]. 4D printing technology is the advanced version of 3D printing and is considered a state-of-the-art manufacturing technique [26]. 4D printing can fabricate any complex part using different materials while maintaining excellent quality, precision, accuracy, and performance capabilities compared to 3D printing techniques [27]. Advanced materials for 4D printing also referred as shape-morphing materials or active origami systems use 3D printing technologies to deposit polymer composites or other materials layer-by-layer for generating 3D products [28–30]. Bioprinters should be chosen carefully by considering the material types and their nature [31]. 4D printing transforms these advanced materials into new dimensions in the presence of different external stimuli including moisture, temperature, light, magnetic field, electric field, biomolecule, pH, cell traction force, and enzymes [32–35]. Nowadays, different 4D printing approaches are utilized which include stereolithography (SLA), fused deposition modeling (FDM), inkjet printing (IJP), digital light processing (DLP), selective laser sintering (SLS), micro-extrusion, and direct ink writing (DIW) [36–40]. Table 1 provides a summary of the different 4D printing approaches applied for the printing of these materials.

In the contemporary world, significant advancements, particularly in the 4D printing technique, have opened the gate for innovations in a plethora of disciplines including aerospace, prototyping, biotechnology, and biomedical sectors [69]. According to the published studies, nearly twenty people lose their lives daily while waiting for the perfectly-matched organs imperative for transplantation and these numbers are continuously increasing worldwide [70–72]. The effect of 4D printing is remarkable in biomedical sector fields, including tissue engineering (TE), scaffolds, and dentistry, which provide a boost to our healthcare systems and improve patients' lives [73–75]. Furthermore, implantation of any organ or tissue regeneration also becomes necessary in the case of an accident. These factors ultimately urge the researchers to think about the development of artificial organs/tissues by incorporating living cells [76–78]. This incepts the bioprinting technology, which relies on bioprinters that have the potential to replicate/print exact stem cells and organs [79].

To date, 4D printing technology has shown tremendous progress in different dynamic micro-environment TE areas, namely tissue cardiac, vascularization, muscle, neural, bone tissue engineering (BTE), and production of vascular stents [80–82]. The major focus of the tissue engineering and regenerative medicine (TERM) approaches is to fully repair or regenerate the traumatized tissues by delivering biocompatible materials to promote the healing mechanism [83–85]. The healing

Fig. 1. A schematic illustration depicting the difference between the 3D/4D printing and 3D/4D bioprinting.

process is attained by combining human cells, biochemical, dynamic, and mechanical signals, and mechanical stabilization which can be achieved through the employment of scaffolds [86–88]. These scaffolds can be fabricated through ceramics, metals, fibers, polymers, or polymer composites [89]. Among these biomaterials, polymers play a significant role in designing and fabricating scaffolds, as they have excellent degradability, biological and chemical properties, and the ability to mimic the native extracellular matrix (ECM), which are vital properties for a biomaterial [90]. Additionally, the programmable dynamic constructs with functionality transform or controlled shape are manufactured by

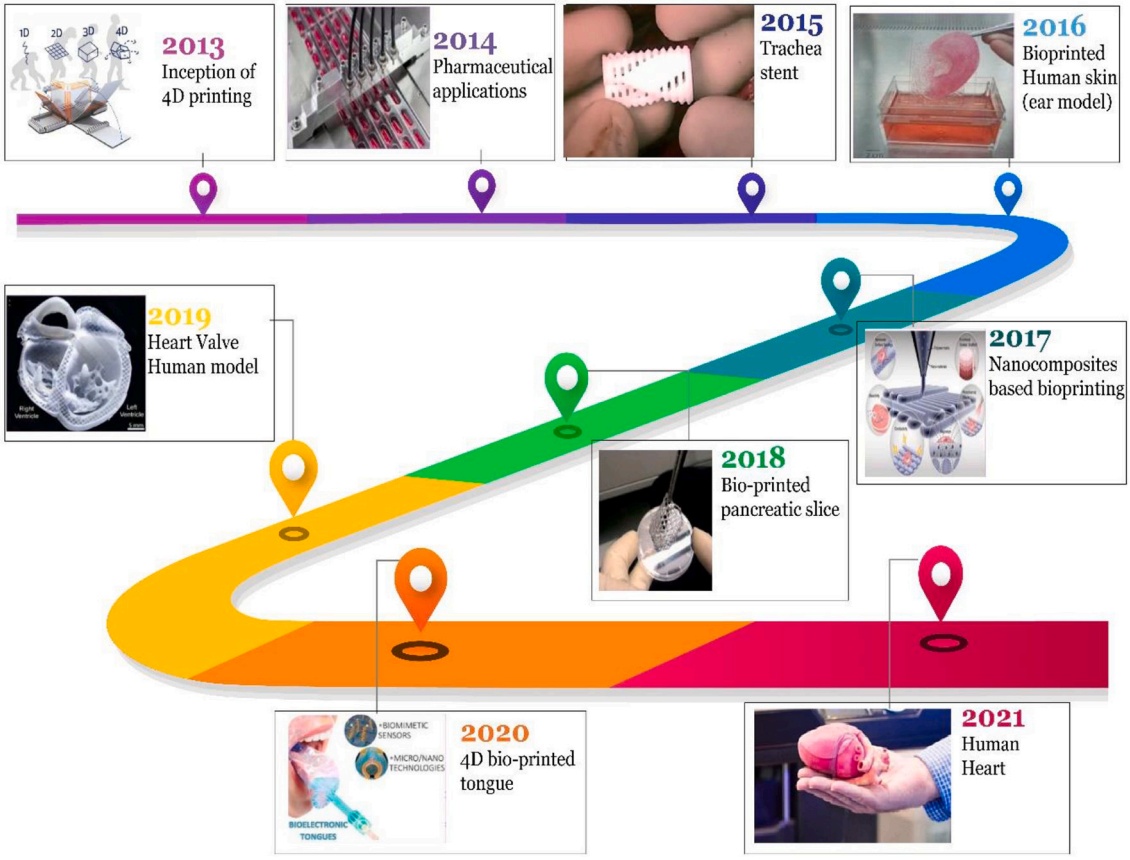


Fig. 2. Year-by-year development in the biomedical field through different 4D bioprinting technology.

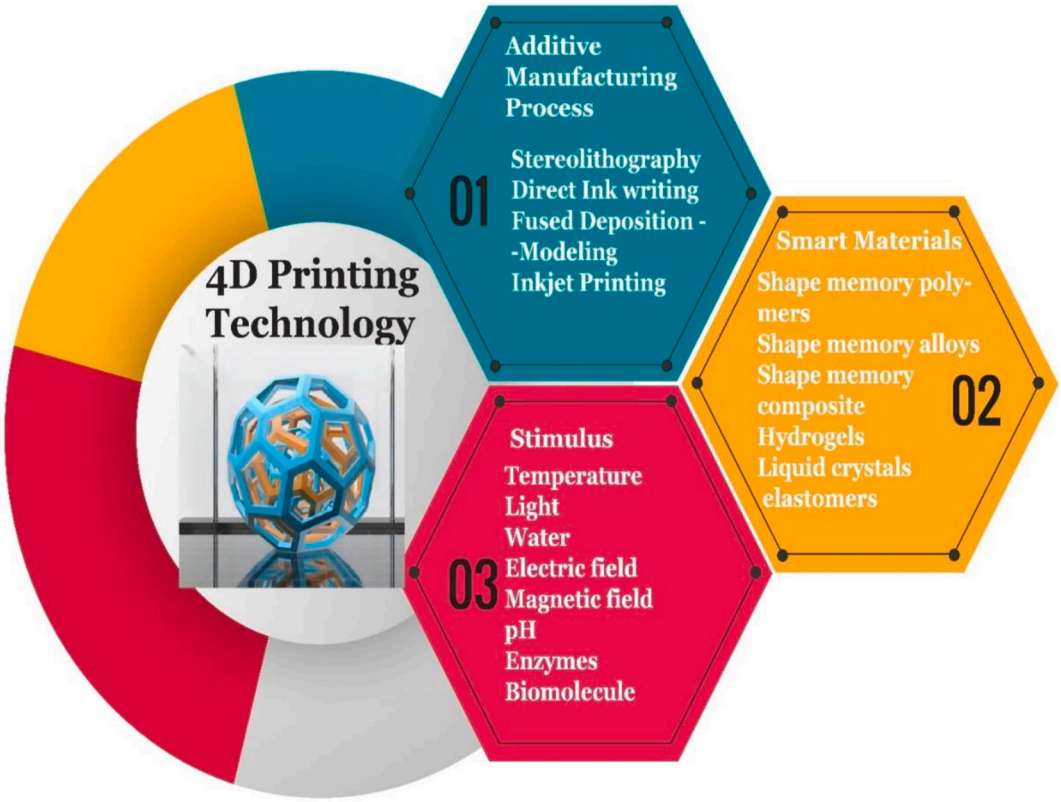


Fig. 3. A schematic diagram depicting different aspects of 4D printing technology including potential materials, printing techniques, and types of stimuli.

using smart polymers of different origins, including synthetic, natural, or hybrid which are molded into shape memory hydrogels and stimuli-responsive materials through 4D printing strategy [91–93].

1.1. Purpose of the review

The primary objective of this review is to address the following research questions (RQs):

RQ1: What is the current status of 4D printing in biomedical fields?

RQ2: What are the different smart materials (SMs), stimuli, and bioprinting techniques employed in 4D printing of biomedical fields?

RQ3: What potential areas in biomedical sectors need to be explored in the foreseeable future for effectively utilizing the 4D bioprinting approach?

2. 4D bioprinting technology

3D bioprinting technology employs bio-ink functional materials to generate intricate 3D cell-laden tissue constructs that mimic native tissues. This approach produces a variety of artificial soft tissues for cartilage, bone, and skin [94–96]. Bioprinting utilizes three primary techniques: extrusion-based, and laser-based, inkjet bioprinting [97–99]. However, the concept of 4D bioprinting implies the deformation of 3D bioprinted structures under external stimulation [100]. Additionally, during post-printing 3D-printed product changes shape in a predefined fashion to achieve the required goal. It permits controlled and precise reproduction of the tissues [101]. Furthermore, it also helps to partially achieve dynamic interaction with native cells [102]. The difference between 4D bioprinting and 3D bioprinting technologies is illustrated in Fig. 1.

The combination of 4D bioprinting techniques and next-generation stimuli-responsive materials develops dynamic 3D-printed biological architectures [103]. In recent years, a significant increase in the published articles related to 4D bioprinting of smart polymers has been observed and it is statistically proved by a recently published review article by Osouli-Bostanabad et al. [104]. The following subsection incorporates important bioactive smart materials which are employed for 4D bioprinting.

2.1. 4D bioprinting materials

4D bioprinting technology has exhibited extraordinary potential in different biomedical applications including drug delivery systems (DDSs), TE, and wound repair [105–108]. It is difficult to fabricate hollow structures and blood vessels through 3D bioprinting [109]. This problem can be solved through 4D bioprinting technology which generates a flat biological structure that folded into the blood tube vessel upon external stimulus [110–112]. Similarly, controlled drug release is made possible through 4D bioprinting in which drugs are delivered at the particular site in response to external stimuli [113–115]**.** Fig. 2 depicts the complete road map of the 4D bioprinting technology.

SMs or stimuli-responsive materials are classified into two major branches: Shape changing materials (SCMs) and shape memory materials (SMMs), stiffness changing materials, and phase changing materials [116–118]. SCMs transform to new shapes upon the variation in the environment and after the removal of external stimuli, these materials regain their initial shape [119]. Thus, the deformation behavior was predetermined in these materials [120]. Whereas, SMMs employ programming steps and use shape-morphing effect to develop printed parts of intricate geometries [121]. These materials are further classified into shape memory alloys (SMAs) and shape memory polymers (SMPs) [122].

Fig. 3 depicts the variety of SMs including SCMs, SMAs, SMPs, shape memory polymer composites (SMPCs), hydrogels, and shape memory elastomers, that have been employed for 4D bioprinting [123–125]. 4D-printed materials depict five types of smart features: shape-memory, self-assembly, self-actuating, self-sensing, and self-healing [126]. In shape-memory, materials transform into predetermined geometry upon

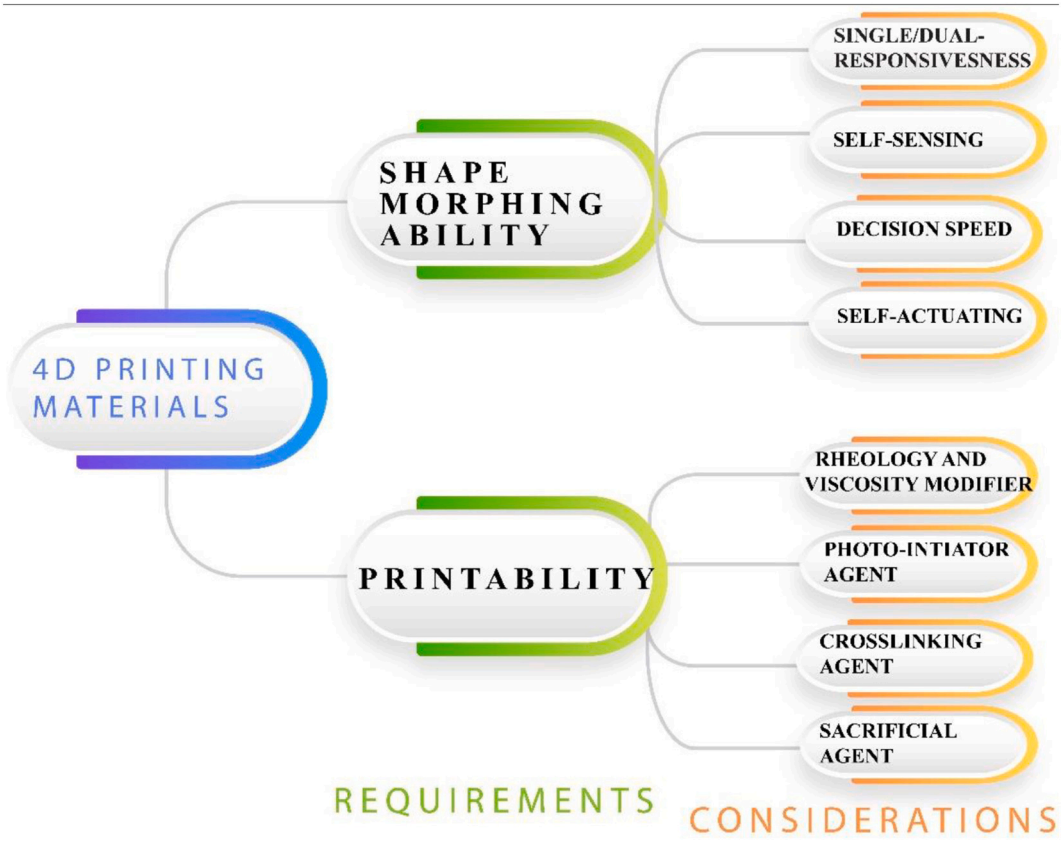


Fig. 4. Material's requirements and considerations for 4D bioprinting.

external stimuli [127]. In self-assembly, external stimuli prompt folding and assembling into pre-programmed geometry [128]. Whereas, in the self-actuating mechanism, external stimuli enforce automated actuation in materials [129]. Self-sensing behavior identifies as well as assesses external stimuli [130]. Automatic restoration of structural damage occurs without external intervention in the self-healing phenomenon [131]. Self-healing hydrogels are extensively utilized in biomedical sectors including TE, wound healing systems, DDS, and 3D bioprinting [132,133]. Furthermore, it is important to understand the functionality of materials for 4D bioprinting technology.

2.2. Functionality of materials

Preprogramming helps materials to provide a deformation response upon external stimuli after 3D bioprinting [134]. Fig. 4 summarize the requirments of materials for biomedical applications. These deformations of the materials are further categorized into one-way, two-way, or multi-way, as illustrated in Fig. 5. In 4D bioprinting, the final shape of the material is precisely controlled by triggering an external stimulus, and materials that transform their shape upon external stimuli are known as stimuli-responsive materials [135]. Numerous external stimuli can be employed including physical (temperature, ultrasound, light, magnetic field, electric field), biological (cell traction forces, enzymes, and glucose), and chemical (pH value, humidity, and biomolecules) [136]. In the following sub-sections, materials sensitive to different external stimuli are elucidated by considering biomedical applications.

2.2.1. Thermo-responsive materials

Thermo-responsive materials can be triggered by changing the internal environment, which transforms their shape [138]. Temperature alteration is an external stimulus applied to achieve the shape-morphing effect [139]. Most sensitive polymer solutions are poly(N-vinylcaprolactam) (PNVCL), poly(N-isopropylacrylamide) (PNIPAM), poly(ethylene glycol) (PEG), collagen, and gelatin (Gel) along with some SMPs including poly(caprolactone triol) (PCL-T), acrylated epoxidized soybean oil (AESO), poly(ε-caprolactone) dimethacrylate, polyurethane (PU), and poly(lactic acid) (PLA) [140–142]. These thermal-sensitive SMPs are commonly used for 4D printing due to their excellent printability and processability. Furthermore, the glass transition temperature of these SMPs is greater than their allowable temperature (a temperature that does not endanger cell viability) [143–145].

Several synthetic-based SMPs exhibit thermal responsive behavior and out of these SMPs, only a few materials possess the intrinsic characteristics to fabricate bio-inks for 4D printing [146]. However, materials whose glass transition temperature is too severe, upper than 58 °C, for the survival of the cells cannot be utilized for the biomedical sector [146]. In another approach, biopolymers and thermo-responsive macromolecules can be applied in combination to trigger the response. Many researchers have developed a variety of thermo-responsive synthetic materials like PNIPAM, which are extensively applied for TERM applications [147]. Similarly, bioactive materials contract or expand, which results in deformation through dissolution with temperature and change in wettability. For instance, Miao et al. [148] printed biocompatible acrylated epoxidized soybean oil (AESO)-based scaffolds with temperature-sensitive shape morphing effect. The authors observed that the scaffolds transformed from their temporary shape to their original shape at normal human body temperature (37 °C). Similarly, Gel is a temperature-sensitive biopolymer that undergoes reversible gel-sol transition through the variation of temperature. They used thermally-responsive Gel and pH-responsive chitin for printing the hierarchical patterns and citrate ion stimuli as the second cross-linker. They observed that the Gel/Chit-H+ hydrogel could shape their change under the cues of stimuli (citrate ion). The results reported by Wen et al. [149] depicted

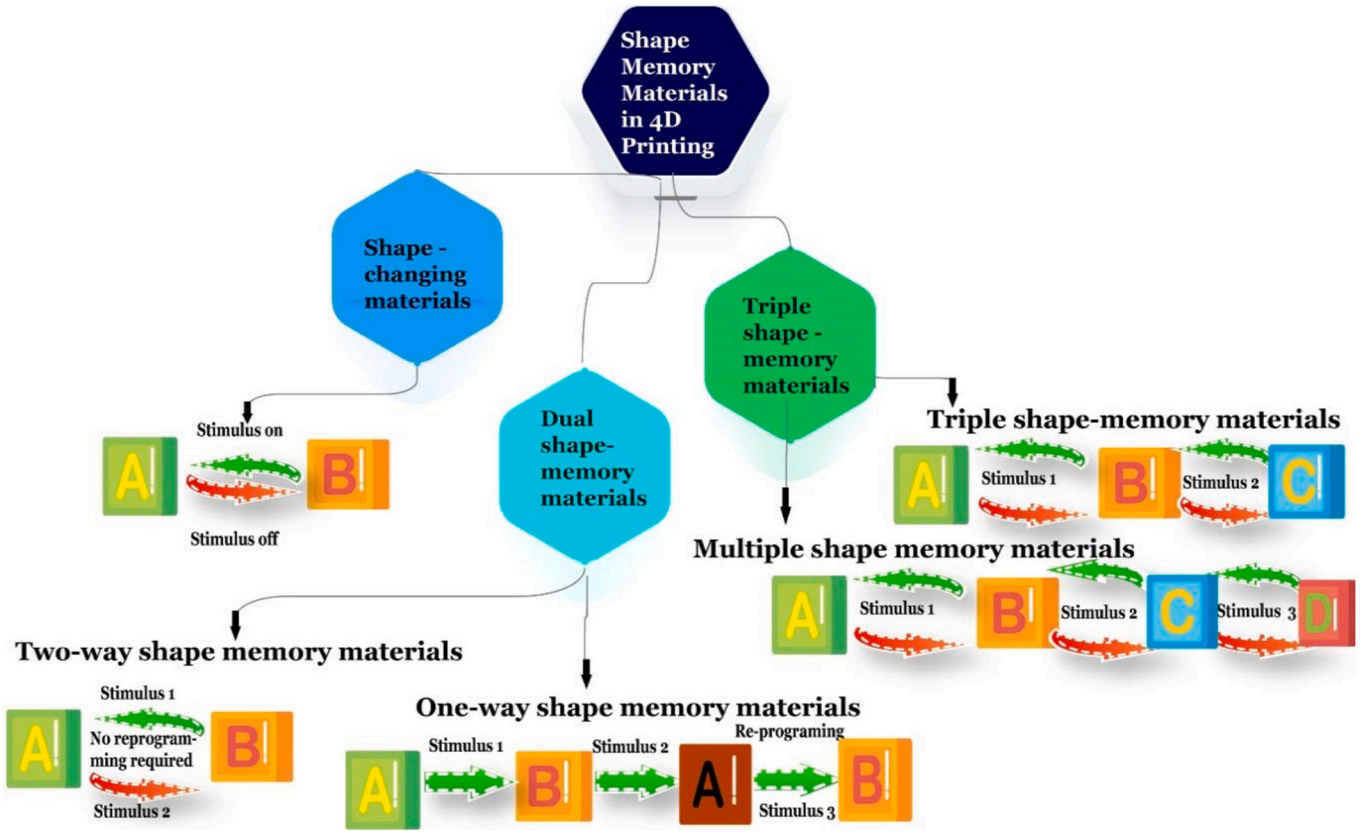


Fig. 5. A schematic illustration depicting the shape morphing mechanisms involved in 4D printing (Adapted with permission from ref. [137], Copyright 2022, Wiley-VCH Gmbh).

that Gel possessed a soluble state above 30 °C and exhibited a gel state below 25 °C. However, the range of these temperature depend upon the gel origin [150].

Bakarich et al. [151] designed a smart valve that controls the flow of water by printing a dynamic Alg/PNIPAm ionic covalent entanglement (ICE) gel ink. The valve closed automatically under hot water exposure, thus reducing the flow rate by 99%, and opened in cold water, as presented in Fig. 6(a). These 4D-printed actuating hydrogel materials potential can be applied in many soft robotics and smart sensing applications. Liu et al. [152] studied the combination of coordination complex of zinc and metformin and pluronic F127-based thermosensitive hydrogel for the healing of traumatic skin defect and burn skin injury. The developed different combinations demonstrated excellent inhibit reactive oxygen species, excellent antibacterial activity, promotes cell proliferation, collagen formation and angiogenesis for effective traumatic skin defect and burn skin injury. Furthermore, the sprayable Pluronic F127 (shown in Fig. 6(b_1)) are promising for drug delivery system used for clinical treatment of skin injury as demonstrated in Fig. 6(b_2)-Fig. 6(b_3). Liu et al. [153] studied the PNIPAM-based thermo-responsive hydrogel modified with CS and Al^{3+}. As the potential smart window materials, the developed hydrogel demonstrate a strong volume phase transition as a result of temperature rises over 20 °C, as presented in Fig. 6(c). Later these prepared hydrogels were used as a novel smart window material to attenuate the dazzling sunset in the afternoon. Zou et al. [154] studied the biocompatibility of in mouse fibroblast cells and sprague dawley rats through incorporating thermosensitive hydroxypropyl chitin (HPCT), N-acetylglucosamine (NAG) and carboxymethyl chitosan (CMCS)-based hydrogel. The prepared hydrogel demonstrated excellent sol-gel transformation as a result of temperature change, as presented in Fig. 6(d_1). Furthermore, the behavior of HPCT/NAG and HPCT/CMCS thermosensitive hydrogels were studied through injection into various areas of diabetic rats as rat pancreatic beta cells (RIN-m5F) carriers, as presented in Fig. 6(d_2)-Fig. 6 (d_3). Reported results showed that HPCT/NAG and HPCT/CMCS hydrogels with RIN-m5F cells improved cell proliferation, delaying cell apoptosis, and facilitated the insulin secretion of RIN-m5F cells in 3D culture. Thus, proposed strategy is promising for the treatment of diabetes via cell engineering. Queiroz et al. [155] studied pluronic F-127-based hydrogels containing mesoporous bioactive glass nanoparticles (NPs) for bone tissue regeneration applications. Thermosensitive response and injectability of the prepared nanocomposites hydrogels were studied, which demonstrated excellent potential for minimally invasive administration and for sol–gel phase transition between two different temperatures, as presented in Fig. 6(e), effective for to be utilized as an injectable system.

2.2.2. *Magneto-responsive materials*

Similarly, a lot of reseach has also been done on the utilization of electric and magnetic fields to trigger certain responses in bioactive materials [156–158]. Magneto-sensitive materials including para- and ferro-magnetic nanoparticles (MNPs) additives can be utilized for DDS [159]. These responsive polymeric materials have exhibited great potential in the biomedical sector. In DDSs, these materials provide minimally invasive and controlled therapeutic action [160]. For instance, the combination of agar/PEG-based hydrogel and Fe_3O_4-based NPs network develops magneto-responsive DDS which treats the traumatized soft tissues [161]. Hydrogels simulated through a magnetic field are excellent candidates to print biomaterials owing to their excellent rheological characteristics [162–164]. Likewise, Zhu et al. [165] developed magneto-responsive based 4D-printed bioproducts through the reinforcement of Fe-based NPs into poly(dimethylsiloxane) (PDMS). Additionally, the magnetized bio-inks can help in controlling the direction of NPs during the bioprinting process, which constructs scaffolds of anisotropic properties.

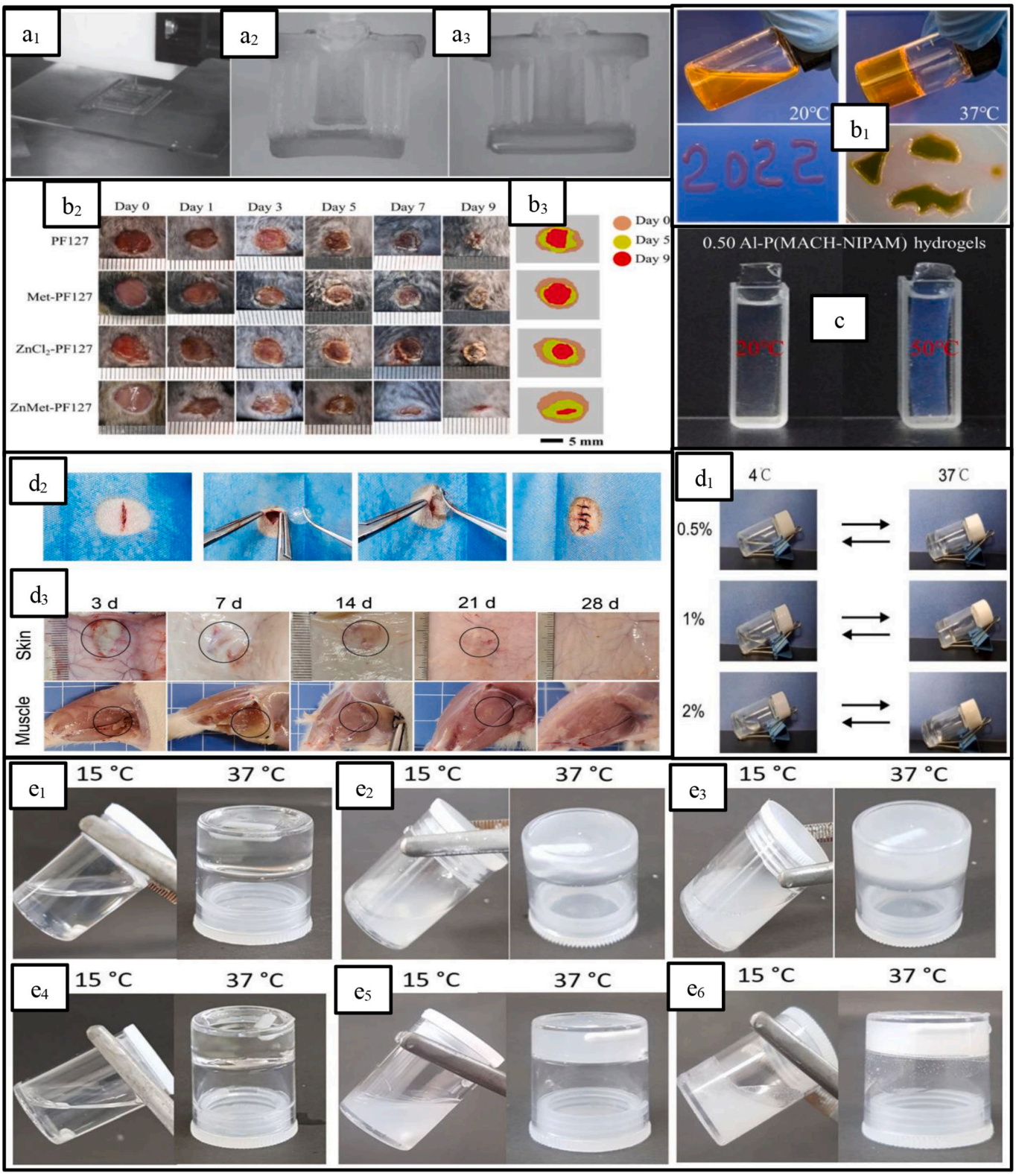


Fig. 6. (a_1) Bioplotter printing of the valve; (a_2- a_3) 4D-printed valve swollen in water, (a_2) At 20^o C. (a_3) At 60^o C (Adapted with permission from ref. [151] Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (b_1) PF127-based thermosensitive hydrogel liquid at low temperatures 20 °C and change able into a semisolid gel at 37 °C due to rise of temperature; (b_2-b_3) Images of healing process of wounds at different time points exhibited that this hydrogel remarkably improves the skin wound healing in comparison to other groups (Adapted with permission from ref. [152]); (c) Picture of 0.50 Al-P(MACH-NIPAM) hydrogel at 20 °C and 50 °C (Adapted with permission from ref. [153] Copyright 2021 Elsevier Ltd); (d_1) Sol-gel transformation as a result of temperature change; (d_2-d_3) HPCT hydrogel implanted in the muscle and subcutaneous tissues along with degradation behavior (Adapted with permission from ref. [154] Copyright 2022 Elsevier B.V.); (e) Thermosensitive response of prepared nanocomposite digital images for different weight percentages of F-127-based hydrogels and bioactive glass NPs at 15 °C and 37 °C (Adapted with permission from ref. [155] Copyright 2022, Springer Science Business Media, LLC, part of Springer Nature).

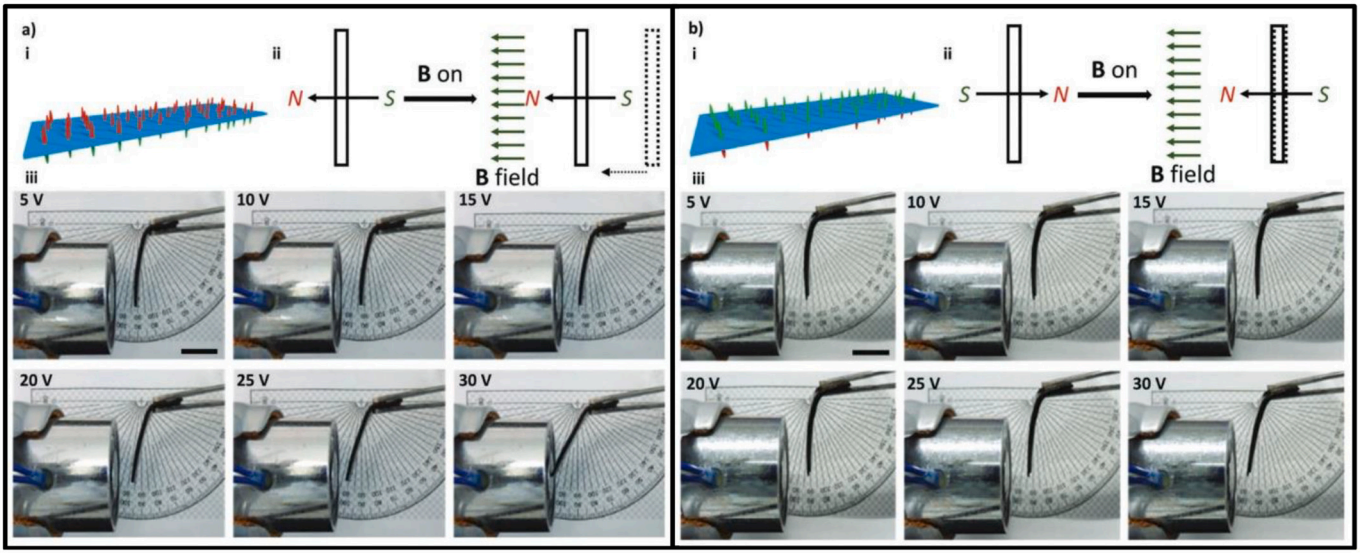


Fig. 7. (a) Deflection control on PEGDA/5 wt% magnetic NPs hydrogel films where the NPs were placed perpendicular to the width of the film and in the direction of the field, depicting deflection towards the magnet as the current of the electromagnet was increased; (b) PEGDA/5 wt% MNPs hydrogel films where the NPs were placed perpendicular to the width of the film antiparallel to the direction of the magnetic field, depicting unresponsiveness until the input voltage of the electromagnet was raised above 25 V (Adapted with permission from ref. [169]).

Other examples of 4D-printed magneto-sensitive polymeric materials developed for TE applications are Fe_3O_4/PCL/mesoporous bioactive glass (MBG)-based scaffolds [166], iron-doped hydroxyapatite (HAP)/PCL-based scaffolds [167], and magneto-nanocomposite scaffolds consisting of Fe_3O_4/polyethylene glycol diacrylate (PEGDA) and Fe_3O_4/PCL [168]. For instance, Kuhnt et al. [169] studied the application of anisotropic Fe_3O_4 magnetic NPs with PEGDA hydrogel though DLP-based 3D printing process. These magnetic NPs demonstrated excellent biocompatibility when directly seeded on top of human mesenchymal stem cells (MSCs), Furthermore, their addition into polymeric nanocomposites, revealed excellent viability higher than 95% of human dermal fibroblasts. Later, the aligning of magnetic NPs with the proper orientations of scaffold permits an unpaired movements, as presented in Fig. 7. Thus, making these magnetic NPs ideal for various biomedical applications particularly for TE.

2.2.3. *Electro-responsive materials*

Electro-responsive materials contain electrically conductive biomaterials including polymers [170]. Bioelectric stimulation of endophyte bioactive materials can help in adjusting the contraction, expansion, or folding by changing the electric field intensity and the internal ambient to influence the direction [171]. Sometimes, these materials incorporate certain electrically conductive additives including carbon nanotubes (CNTs), graphene, and other NPs [172]. For instance, Okuzaki et al. [173] developed an origami robot through 4D printing of electro-sensitive polypyrrole-based organic polymer. Currently, these bioactive materials are investigated to develop constructs for muscle and neural TE applications [174]. Additionally, conductive polymer-based hydrogels exhibit excellent printing performance and biocompatibility and could be chosen for 4D printing of biomaterials.

2.2.4. *Photo-responsive materials*

Photo-responsive materials permit the use of light stimulus to modify the size or shape of the constructs, including bending, contraction, or volume transformations. These materials include polymers or polymers containing stilbene, derivatives of nitrobenzene, azobenzene, fulgide, spiropyran, or photosensitive-nanomaterials [175]. Photo-responsive polymeric materials are fabricated by embedding chromophores in polymer resins. Similarly, these materials can also be developed by the addition of photosensitive-nanomaterials into polymers [176]. The response of the system could be irreversible or reversible depending on the chromophore type. Irreversible photo-responsive polymeric materials are also called photodegradable polymers which find their utilization in the development of DDS [177]. However, 4D bioprinting of polymeric materials that shrink, swell, or self-assemble upon photo-triggering requires insightful exploration for TE applications. Recently, light-sensitive polymers were developed by functionalizing PNIPAM hydrogels and spirobenzopyran [178].

2.2.5. *Moisture-responsive materials*

Moisture-responsive materials usually absorb or lose moisture in the humid environment or cell culture medium and swell, fold, twist, or deform in other forms [179]. These swelling and deswelling mechanisms of these SMs are helpful for actuating and soft robotics applications. For example, Zhang et al. [180] fabricated moisture-sensitive material through the modification of microcrystalline cellulose (MCC) with stearoyl moieties. The developed 4D-printed material could bend when placed in a moist environment. Kim et al. [181] by employing UV-assisted direct-ink-writing-based 3D printing, fabricated smart structures which could change their shape in the presence of moisture. The printed structures changed their shape in moist conditions and recovered their original shape in dry conditions. This characteristic can also be explored in other biopolymers for extending their possible use in the biomedical sector. Similarly, several other polymeric materials, including cellulose, silk fibroin, PU and PEGDA, utilize desorption or sorption of humidity as the actuating responsive force [182,183]. For instance, Ganesan et al. [184] studied vapor-responsive behavior of silk fibroin films with unusual multiple bidirectional macroscale actuation in a reversible manner such as an upward bending and downward bending were observed for water and ethanol vapor-based stimulus. This is due to water-induced minuscule expansion and contraction of the film surface enabling fully reversible large-scale actuation. Furthermore, 3D shape morphing capability of the actuator by triggering an undulating wavelike motion though preprogrammed water and ethanol vapor-based stimulus conditions, as presented in Fig. 8(a). The proposed methodology has potential to use further in development of fluid pumping in lab-on-a-chip microfluidic devices. Cui et al. [185] fabricated tendril-inspired hydrogel artificial muscles by incorporating tunicate cellulose nanocrystals (TCNCs) into polymeric networks through host-guest interactions to reinforce the hydrogel. These

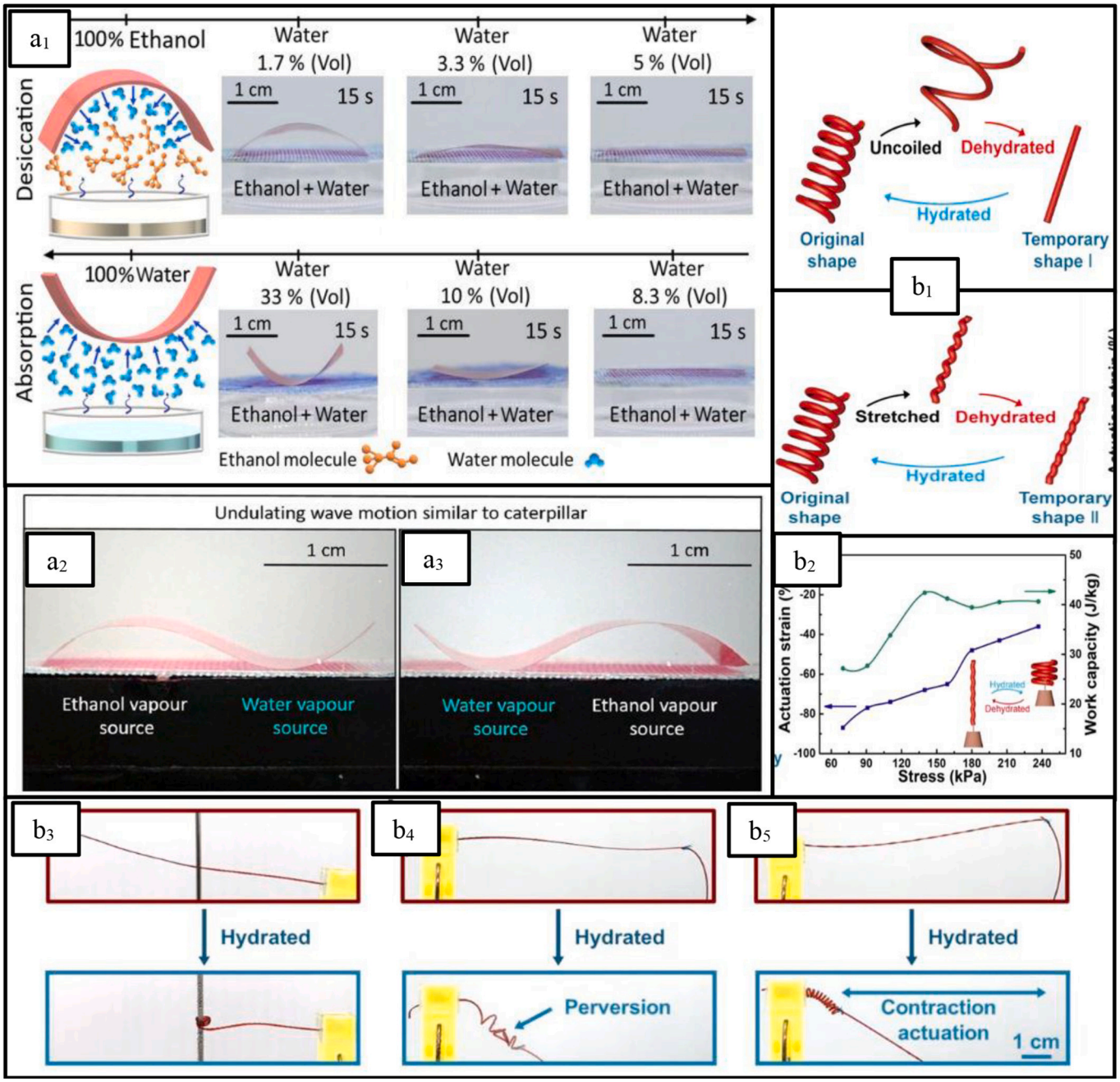


Fig. 8. (a_1) Shape morphing behavior of the silk fibroin film under mixtures of both ethanol and water -based stimulus at different cocentrations; (a_2-a_3) Demonstrating the caterpillar/ undulating wave motion of flat silk fibroin film changes its shape to a waveform under to water and ethanol vapor simultaneously in a preprogrammed manner (Adapted with permission from ref. [184] Copyright 2022 American Chemical Society); (b_1) Schematic depictions of the shape memory effect of homochiral hydrogels with various temporary shapes; (b_2) Actuation strain and work capacity versus applied stress for the homochiral hydrogel with temporary shape II; (b_3-b_5) Homochiral hydrogel with different temporary shapes in response to water spray, (b_3) One-end-tethered homochiral hydrogel with temporary shape I; (b_4) Two-end-tethered homochiral hydrogel with temporary shape I; (b_5) Two-end-tethered homochiral hydrogel with temporary shape II (Adapted with permission from ref. [185] Copyright 2021 American Chemical Society).

hydrogel muscles showed a large actuation rate, actuation strain, and shape memory behavior under specific stimuli. The actuation characteristics of hydrogel muscles were dependent o their chirality, applied stress, twist density and temporary shape, as explained in Fig. 8(b). Thus, developed hydrogels offer many opportunities for biomedical sector due to their comparable water content and contractile work ability similar to the natural muscles.

2.2.6. *pH-responsive materials*

pH-responsive biomaterials are biologically active materials that comprise different functional chemical groups, including pyridine, carboxyl, sulfonic phosphate, or acid [186,187]. When the environmental pH changes, these chemical groups respond by delivering or gaining protons and triggering biomaterials to collapse or swell [188]. These materials are divided into two types: basic polymers (contain $-NH_2$ group) and acidic polymers (contain $-SO_3H$ and $-$ COOH groups) [189]. The polymers which are mainly altered through pH are natural biopolymers including hyaluronic acid (HA), collagen, alginate (Alg), Gel, keratin and chitosan (CS), or synthetic polymers like poly(histidine) (PHIS), poly(acrylic acid) (PAA), poly(L-glutamic acid), and poly

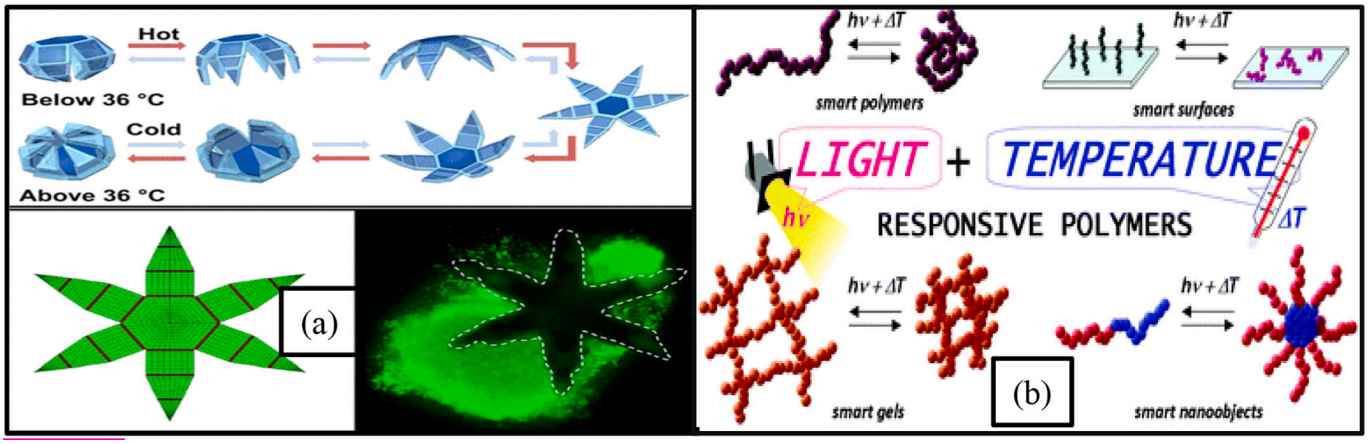


Fig. 9. (a) Thermo-magnetic responsive microgripper printed by using PNIPAM-AAc-based hydrogel and Fe_3O_4-based NPs (Adapted with permission from ref. [207] Copyright 2015 American Chemical Society); (b) Photo-thermo responsive hydrogels (Adapted with permission from ref. [208] Copyright 2013 Royal Society of Chemistry).

(aspartic acid) (PASP) [190–192]. The fabrication of complex printed hydrogels will be helpful for developing intricate tissues for imparting vascularization functionalities [193]. Due to their unique properties, pH-sensitive materials have also been extensively applied in various biomedical applications including gene delivery systems, DDSs, and glucose sensors [194]. Additionally, there is a difference between the pH levels in the different parts of the human body and the sensitiveness of these polymeric materials can be utilized in TE applications [195].

2.2.7. *Biological-responsive materials*

Biological-responsive materials use biological stimuli like bio-enzymes, glucose, and biomolecules [196]. It is an intriguingly employed idea in which certain bio-enzymes cleave peptide sequences and biomolecules, and induce alterations in the polymers causing them to swell [197]. This shape-morphing effect can be extensively applied in TERM-related applications [198]. For instance, Devillard et al. [199] fabricated bioinspired hydrogels which were triggered by two bio-enzymes, thrombin and alkaline phosphatase. This developed fibrin deposition and calcification on the 4D-printed product. The functionalized hydrogels can also be fabricated through 4D printing, which reacts to biological signals [200]. When considering 4D printing, the combination of biological responses with other physical or chemical responses requires insightful exploration.

2.2.8. *Multi-responsive materials*

Some materials are sensitive to multiple-stimuli and use a combination of them [201]. These materials are popular among the scientific community dual to their multi-dimensional and diverse responses [202]. Similarly, multi-sensitive polymeric materials have the ability to undergo chemical and conformational changes and have found their applications in TERM, DDS, and soft robotics [203]. For example, a dual-stimuli 3-azido-2-hydroxypropyl methacrylate-based polymers sensitive to PH and temperature was fabricated by Cai et al. [204] for their possible utilization in the biomedical sector. Similarly, Li et al. [205] synthesised poly(NIPAAm-*co*-PAA-co-MA-PEG-co-HEMAoTMC) hydrogels by free radical copolymerization, which was duel-responsive hydrogels for cardiac tissues that responded to pH and temperature. The results indicated that this hydrogel solidified at pH (~7.4) and 37 °C but didn't solidify at pH (6–7) and 37 °C. Also, they observed that encapsulated the cardiosphere derived cells could survive for one week.

Similarly, thermo-magneto sensitive polymeric materials have been used for surgical excision [206]. Breger et al. [207] printed thermo-magnetic responsive microgripper by using poly(N-isopropyl acrylamide-*co*-acrylic acid) (PNIPAM-AAc) and Fe_3O_4-based NPs, as illustrated in Fig. 9(a). Similarly, the incorporation of azobenzene chromophore in N-isopropylacrylamide thermo-responsive polymeric materials makes them light and temperature-sensitive materials [208], as shown in Fig. 9(b). In another interesting study, Breuer et al. [209] incorporated graphene oxide (GO) into PNIPAM-based hydrogel to develop duel-sensitive materials which could be utilized in DDS. Triple-responsive polymeric materials were developed by different researchers which are responsive to physical, chemical, and biological stimuli [210–212]. These multi-functional polymers can be potentially applied in biomedical fields for TE, drug delivery, and bio-adhesives [213].

Meurer et al. [214] demonstrated triple shape memory effect (TSME) of metallopolymer networks due to switching of the two temporary shapes as a result of activating and deactivating metal–ligand interactions of different stability. Reported results revealed that the crosslinked polymer containing Fe exhibited excellent recovery rates. While polymer containing Fe/Zn and Co/Zn showed the highest strain fixity rates for the first fixation step, as presented in Fig. 10(a). Zeng et al. [215] developed TPU/PLA/poly (propylene carbonate) (PPC) ternary shape-memory blends. Differences in compatibility, surface tension, and viscosity of each component, produced a special co-continuous structure between TPU and compound. Furthermore, the morphology of PPC and PLA act as switches and the interfacial area between compound and TPU changeable through varying the composition of LPC, thus producing tunable dual- and TSME. Excellent TSME performance, as presented in Fig. 10(b), was due to phase morphology and thermal-mechanical conditions particularly for the blend containing 15 wt% PLA. Yang et al. [216] prepared shape memory poly(aryl ether ketone) (PAEK) and grafted carboxylic acid pyridine zwitterions to study the TSME of zwitterionic PAEK material. Through the interaction between water molecules and carboxylic acid pyridine zwitterions the controllable reconfiguration behaviors were observed. Moreover, the excellent TSME of sample were achieved as a result of water absorption. Furthermore, the temporary shape-based sample were recovered to the original shape, as a result of two stages (110 °C and 140 °C) and after the programmable shape fixation processes, as illustrated in Fig. 10(c). These water-responsive, reconfigurable, and TSME of zwitterionic PAEK potential to be used as smart sensors and actuators. In another study, Wan et al. [217] studied multiple shape changing behavior of poly(D,L-lactide-*co*-trimethylene carbonate) (PLMC)/poly(trimethylene carbonate) (PTMC)/Fe_3O_4 multi-material under triple stimuli. The addition of Fe_3O_4 NPs was made these multiple material effective for magnetic stimulus. Finally, these multiple-SMP and its nanocomposites demonstrated excellent shape changing behavior with more degrees of freedom transformation under simultaneously thermo- and magnetic- stimulus, as presented in Fig. 10(d), and also exihibited excellent biocompatibility.

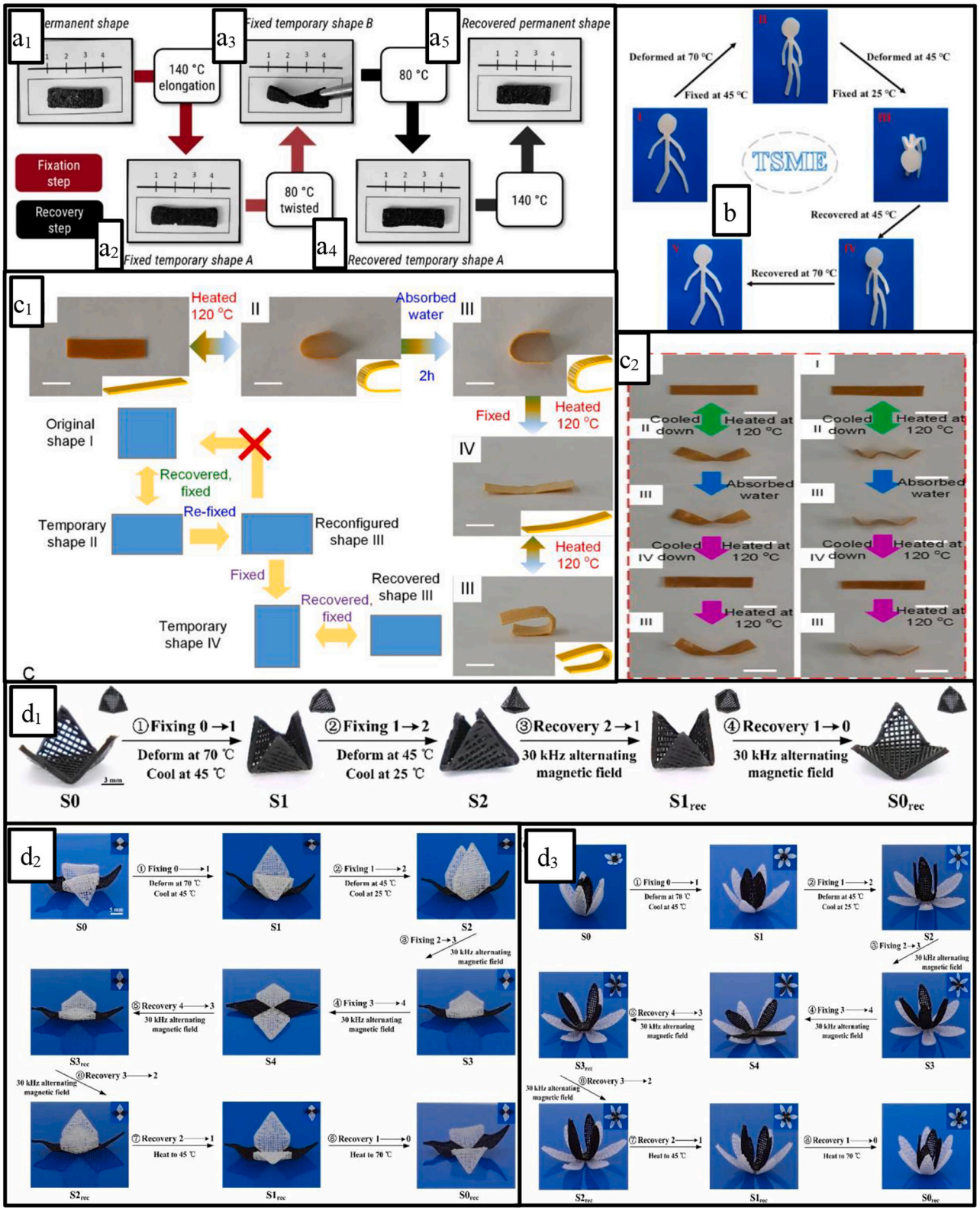
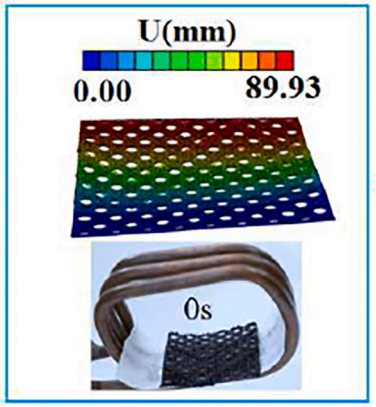
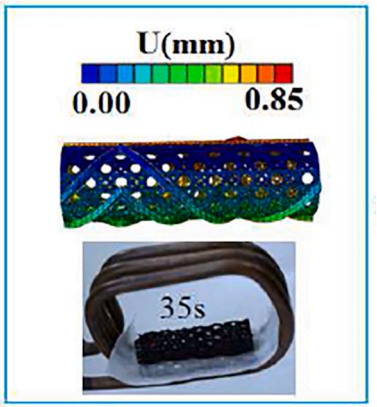
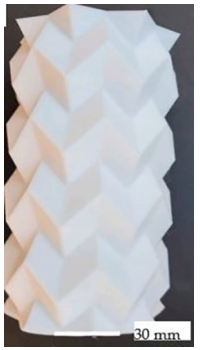


Fig. 10. (a) TSME of crosslinker polymer containing Co/Zn through different fixed and recovered shapes (Adapted with permission from ref. [214]); (b) TSME of the sample containing 15 wt% of PLA (Adapted with permission from ref. [215] Copyright 2022 Elsevier Ltd.); (c_1) Illustration of TSME of PAEK-PS after immersing in water for 2 h; (c_2) Diverse deformation actions (Adapted with permission from ref. [216] Copyright 2022 American Chemical Society); (d) Schematic illustration of TSME on 4D-printed structure under an external stimulus of heat, magnetic field or both. Actual images of multiple and selective shape transformation of a 4D-printed samples; (d_1) Tetrahedron under a 30 kHz alternating magnetic field; (d_2) Multi-material crane and (d_3) Multimaterial flower under the alternating magnetic field and later immersed in a water bath (Adapted with permission from ref. [217] Copyright 2022 Elsevier B.V.).

Table 2
A summary of recent work on 4D printing of smart polymers along with their mechanical properties.

4D printing technique	Printed material	Printing Parameters	External stimuli	Printed model	Stimulated configuration	Role in biomedical application	Ref.
FDM	PLA/Fe_3O_4-based composites	Nozzle diameter = 0.4 mm Printing speed = 50 mm/min Printing temperature = 210 °C Layer thickness = 0.8 mm	Magnetic field			Tracheal stent	[223]
FDM	PLA-based origami structures	Layer thickness = 0.15 mm	Temperature			Biocompatible scaffolds	[224]
FDM	PU-based polymer	Nozzle diameter = 0.4 mm Printing speed = 20 mm/s Layer thickness = 0.2 mm	Temperature			Self-coiling/ deploying stents.	[225]
FDM	Unsaturated PLA-PCL copolymer	Nozzle diameter = 0.4 mm Printing temperature =	Temperature			Elbow protection	[226]

(*continued on next page*)

Table 2 (*continued*)

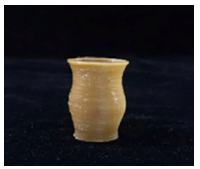
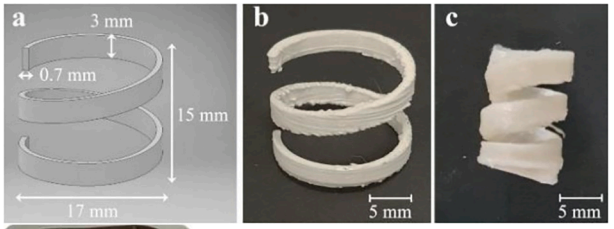
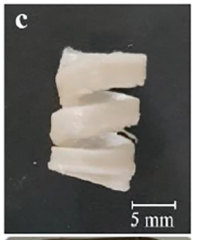
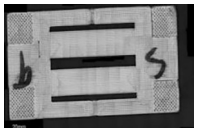
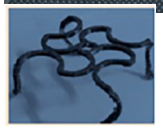
4D printing technique	Printed material	Printing Parameters	External stimuli	Printed model	Stimulated configuration	Role in biomedical application	Ref.
		210 °C Printing speed = (4.5–45) mm/s					
FDM	PVA/GLY/ALP	Nozzle diameter = 0.5 mm Printing temperature = 200 °C and 230 °C Printing speed = 23 mm/s and 50 mm/s	Temperature			Design of expandable system for gastric retention	[227]
FDM	PLA/Fe_3O_4-based composites	Printing speed = 33 mm/s Nozzle temperature = 205 °C Layer thickness = 0.2 mm	Magnetic field			Tracheal stents (Medical treatment device)	[202]
FDM	PLA	Printing temperature = 195 °C Printing line height = 50 μm Printing line width = 0.4 mm	Temperature			Adductor muscle (bio-inspired 4D structures)	[228]
FDM	PLA-based MNCs	Printing speed = 5 mm/s Nozzle temperature = 5 °C	Temperature + magnetic field			Treatment of LAAO	[229]
FDM	PLA/ PBS/GO	Printing temperature = 210 °C Printing speed = 10 mm/s Printing line height = 100 μm	Temperature			Tracheal stent	[136]

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Table 2 (*continued*)

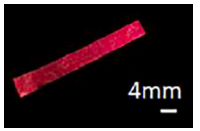
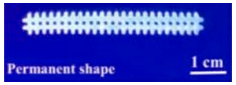
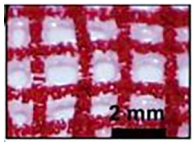
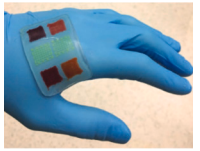
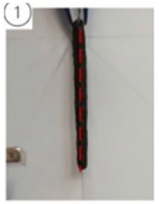
4D printing technique	Printed material	Printing Parameters	External stimuli	Printed model	Stimulated configuration	Role in biomedical application	Ref.
FDM	PHDI/PCL triol	Nozzle size = 300 μm Layer thickness = 50 μm	Temperature			Muscle tissue regeneration	[230]
Extrusion	PGDA-based polymer	Nozzle diameter = 600 μm	Temperature			Arterial grafting	[231]
Extrusion	Alginate glycerin hydrogel	Single extruder was used flow rate = 22 μL min^{-1} Printing speed = 5 mm s^{-1}	pH			Skin dressing (color changing)	[232]
Extrusion	Hydrogels	Pressure < 10 kPa	Magnetic field			Development of soft biocompatible robotics	[233]
Extrusion	HAP/collagen	Pneumatic pressure = 200–300 kPa Moving speed of nozzle = 10 mm/s	Water			Bone tissue regeneration	[234]

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Table 2 (*continued*)

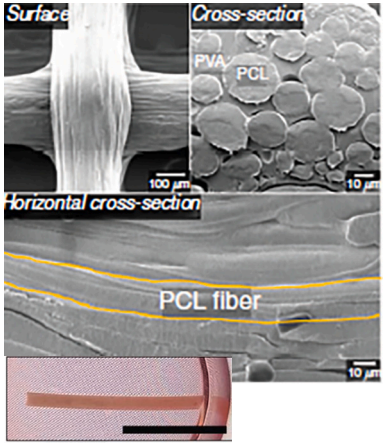
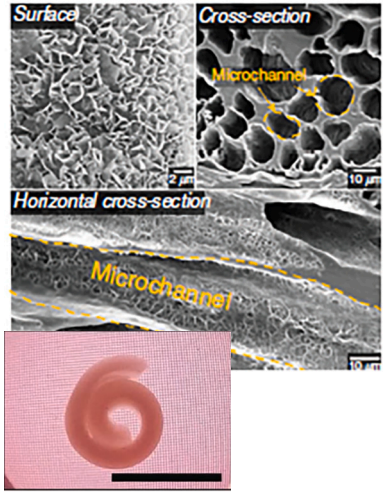
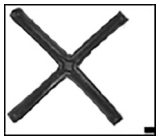
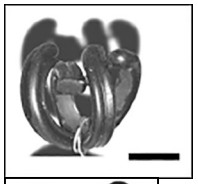
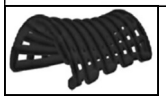
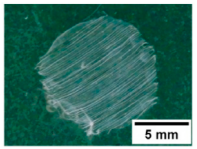
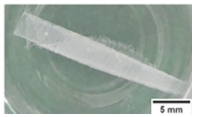
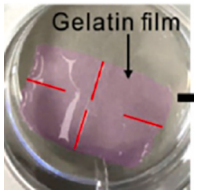
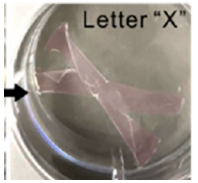
4D printing technique	Printed material	Printing Parameters	External stimuli	Printed model	Stimulated configuration	Role in biomedical application	Ref.
Extrusion	GelMA/oxidized MA	–	Water			Cartilage tissue regeneration	[235]
Extrusion	PU	Printing speed = 30 mm/s Printing line height = 180 μm	Water + temperature			DDS	[236]
Extrusion	PDA/Alg	–	NIR			Tissue regeneration	[237]
Extrusion+ melt-electrowriting	PCL/SA-MA	Flow rate = 5 mm s^{-1} Pressure = 0.4 bar	pH			Skeletal muscle scaffold	[238]
Electrically assisted-Extrusion	GelMA	Pneumatic pressure = 10 kPa	Water			Brian tissue regeneration	[239]

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Table 2 (*continued*)

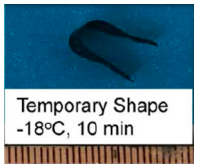
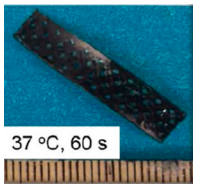
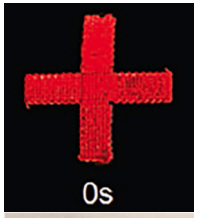
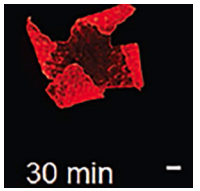
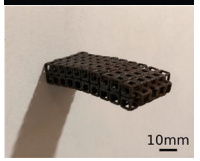
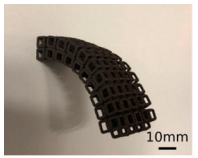
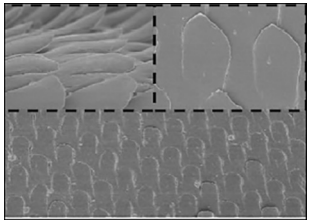
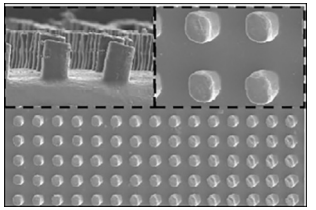
4D printing technique	Printed material	Printing Parameters	External stimuli	Printed model	Stimulated configuration	Role in biomedical application	Ref.
Laser printing	PNIPAM/sodium alginate/agarose	–	Temperature			Smart bandages for chronic wounds	[240]
SLA	AESO	UV laser = 355 nm Print speed =10 to 80 mm/s Laser frequency = 8000 to 20,000 Hz) Thickness < 100 µm	Temperature			Biocompatible scaffolds	[148]
SLA	PCLMA	UV laser = 405 nm Thickness = 150 µm	Temperature			Tracheal stent	[241]
SLA	Graphene/AESO	UV laser = 355 nm Thickness = 200 µm	Temperature + biological			Nerve grafting	[174]
SLS	Nylon-12/ ferrofluid	–	Magnetic			Wearable assistive device	[242]
DLP	PCLDA-based polymer	Layer thickness = 0.4 mm Sample shape = 4 mm × 1 mm	Temperature			Bone defect repairing (controling cell fate)	[243]
DLP	PPF star polymers	405 nm UV light	Temperature				[244]

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Table 2 (*continued*)

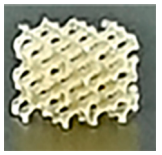
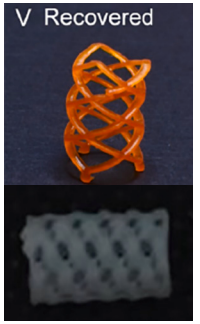
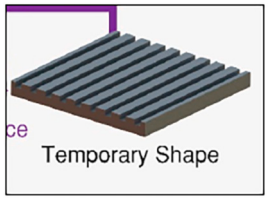
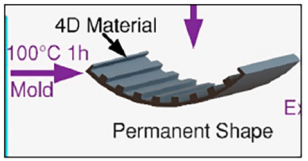
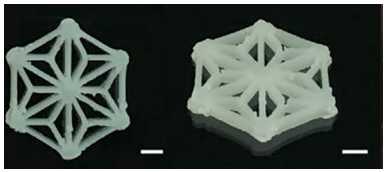
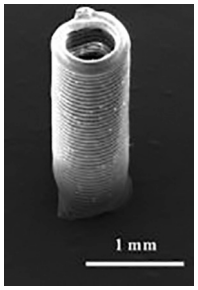
4D printing technique	Printed material	Printing Parameters	External stimuli	Printed model	Stimulated configuration	Role in biomedical application	Ref.
						Large bone defect regeneration	
DLP	PCL/PEGDMA/ BMA	365 nm LED UV light projector	Temperature			Tracheal stent	[245]
DLP	βCD-g-PCL	365 nm LED UV light projector Layer thickness = 0.16 mm	Temperature			Tracheal stent	[246]
DLP	PEGDA + graphene	365–405 nm LED UV light projector	Light			Cardiac tissue regeneration	[247]
DIW	Protein-based hydrogel	–	Temperature + pH+ Enzymatic degradation		–	Degradation of the bovine serum albumin network	[248]
DIW	Fe_3O_4/ benzophenone/ PLA	Printing pressure = 1.75 MPa Printing speed = 0.4 mm/s	Magnetic field		–	Cardiovascular implant	[249]
DIW			Temperature				[250]

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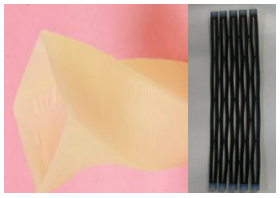
Table 2 (*continued*)

4D printing technique	Printed material	Printing Parameters	External stimuli	Printed model	Stimulated configuration	Role in biomedical application	Ref.
	Semi-IPN elastomer composites	Nozzle diameters =600 μm Temperature near 70 °C. Pressure = 14 psi Printing speed = 10 mm/s				Vascular repair device	
IJP	SMP composites	–	Temperature			Stents	[251]

2.3. SMPs-based SMs

SMPs exhibits better shape recovery feature compared to the SMAs and possess excellent compatibility with modern manufacturing techniques including 4D printing which have continuously enhanced their utilization in biomedical applications including cardiac patches, stents, cardiovascular implants, orthopedic implants, actuators, skin dressings, biosensors, scaffolds, and splint [218–221]. Therefore, these polymers can be adjusted to provide tunable properties for patient-specific applications [222]. Recently, a lot of research was dedicated to the in-vitro and in-vivo responses of the 4D bio-printed SMP products. Table 2 depicts 4D bioprinting approaches, resolution, utilized polymeric materials and hydrogels, and external/internal stimuli employed for developing 4D-printed products for specific biomedical applications.

Cen et al. [252] studied 4D printing of a pickering emulsion stabilized by citrus pectin/β-Cyclodextrin (β-CD) complexes. Results showed that the emulsion demonstrated 4D printing capabilities due to addition of pH-sensitive curcumin. Furthermore, the decomposition of various ions such as HCO_3^- into CO_3^- results in higher pH values after heating, and printed samples changes colors from yellowish to red and the chroma of the samples changed based on various geometric values, as presented in Fig. 11(a). Zhao et al. [253] proposed origami designed-based stents having self-assembly through 4D printing. The shrinkage ratios of various stents-based on different helical angles and unit cells were calculated. Results showed shrinkage ratio of the stents were improved as a result of introducing helical angles into the structures. Furthermore, the changes the configuration of the flexure hinge, improvement in the structural flexibility, and the shrinkage ratio due to introducing lightweight design. Fig. 11(b) showing comparison between the initial and folded states of the stent along with the depiction of self-assembly stimulated by heat, thus making them to use further in tissue engineering applications. Zhang et al. [254] designed 3D functional microarchitectures using pH-responsive hydrogel by holographically shifted femtosecond multifoci. The fabricated microcage array demonstrated high performance target capturing triggered by environmental pH, as presented in Fig. 11(c). Furthermore, the fabricated scaffolds served as arrayed analytical platforms for monitoring the cell patterns in normal or changeable living spaces or demonstrating the anticancer effects of loaded drugs. Thus, proposed methodology have potential to use in manufacturing of hydrogel-based functional microstructures for micro-object manipulation. Miksch et al. [255] studied PEG-based synthetic microgels with different degrees of degradability for fabrication of porous microgel scaffolds using particle jamming and extrusion-based 3D printing, as presented in Fig. 11(d_1). Furthermore, large-scale 3D culture in a macroporous hydrogel was demonstrated due to the high-throughput direct encapsulation of cells within printable microgels. Moreover, the printed scaffolds are promising materials for 2.5D and 3D tissue culture due to unprecedented spatiotemporal control over the properties of printed microporous annealed particle, as presented in Fig. 11(d_2).

Jang et al. [256] developed semicrystalline shape-morphing polymer of controlled shape programmability. An anisotropic stimulus response in the films were developed due to dark and bright regions during photopolymerization via a projector. Moreover, the spatially patterning the crystal orientation results in developments of different complex 3D shapes including a helical coil, a cone, a coil with a handedness inversion, a twisting flower and a saddle, as presented in Fig. 12(a). The actuation temperature controlled by varying the chemical composition ratio. The proposed methodology are promising for wide range of applications such as deployable electronics to morphing biomedical devices. Zhang et al. [257] reported a mechanically robust and quick shape morphing ability due to volatilization of a non-fully-reacted, volatile component in a partially cured cross-linking network obtained from photopolymerization. Various complex shape transformations, such as a buckyball self-folding from a 2D hexagonal lattice sheet and multiple pop-up structures transforming from their initial compact

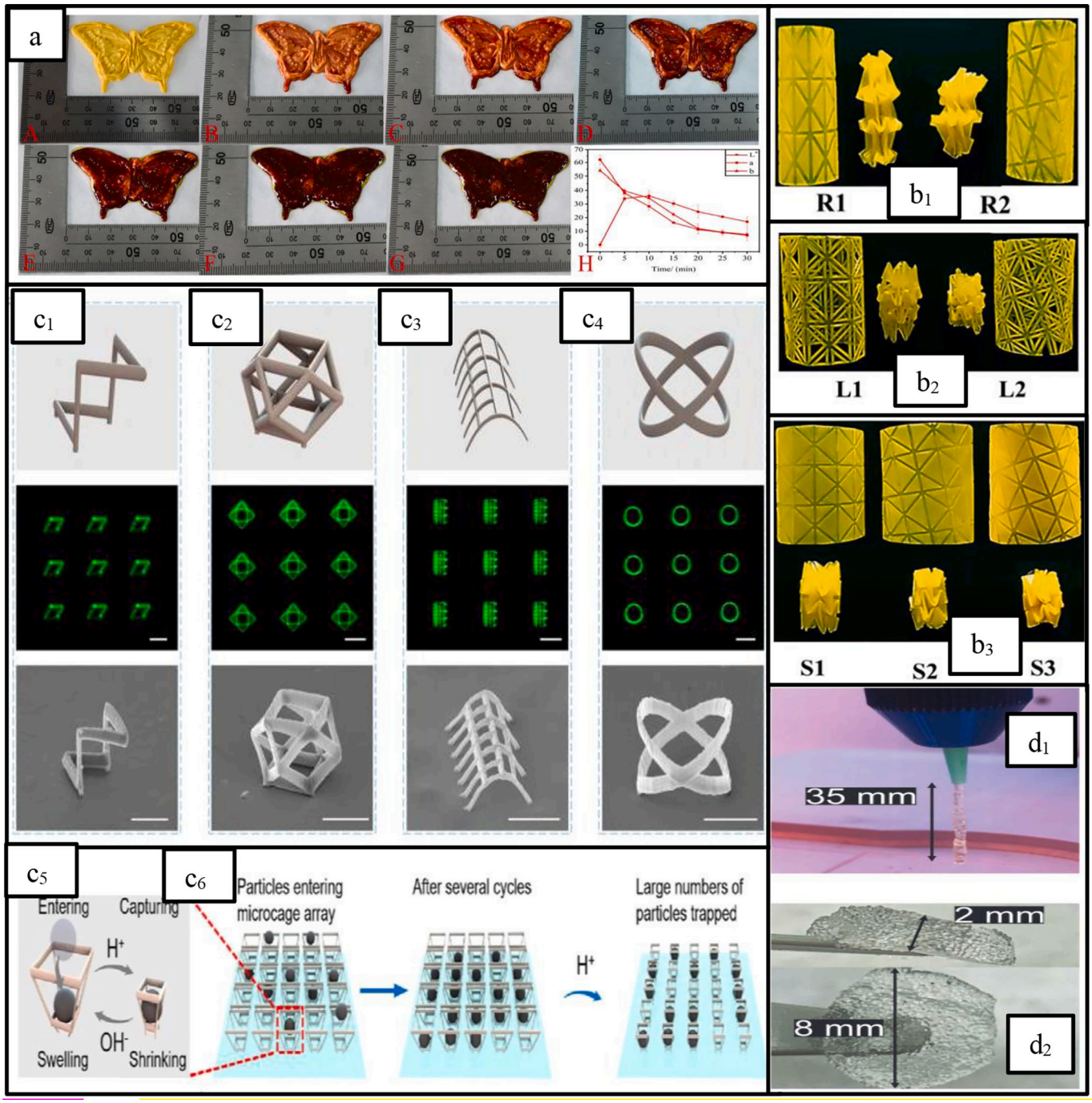


Fig. 11. (a) Photographs of various samples and associated chroma values after heating at various time. A, B, C, D, E, F, G, and H reveals the chroma values of the sample (Adapted with permission from ref. [252] Copyright 2022 Elsevier B.V.); (b) Comparison of various stents before and after folding (Adapted with permission from ref. [253] Copyright 2022 Elsevier Ltd.); (c_1-c_4) Various microarchitectures used for capturing of microparticles through pH-responsive hydrogel; (c_5) Schematic illustration depicting a single microcage swells and shrinks for capturing a microparticle; (c_6) Schematic illustration of the capturing procedure of the microcage array. HCl solution was added to trap particles within the microcages after large amounts of particles enter the structures in several dropping cycles (Adapted with permission from ref. [254] Copyright 2022 American Chemical Society); (d_1) Printing of microgel through an 18 gauge conical tip; (d_2) Annealing by secondary photocross-linking afforded large, scaffolds made from tens of thousands of microgels (Adapted with permission from ref. [255] Copyright 2022 Wiley-VCH GmbH).

configurations were observed, as presented in Fig. 12(b_1)-Fig. 12(b_3), due to volume shrinkage caused by the loss of the volatile component. These miura-ori structure hold more than 1600 times its weight, as presented in Fig. 12(b_4). Yang et al. [258] fabricated smart materials through integration of the metal coordination bonds into shape memory PAEK for demonstrating multifunctionalities. The excellent shape memory behavior in terms of high recovery ratio (over 98%) and fixity ratio (over 98%) were observed as a result of tuning the metal ion content and species, which resembles with the synergic effect of the intrinsic motion capability of PAEK matrix and the cracking-recombination of coordination bonds. Furthermore, PAEK material demonstrated the excellent self-healing and reprocessing performances, due to the dynamic cracking-recombination of coordination bonds, as shown in Fig. 12(c). Hamzehei et al. [259] introduced novel 3D meta-materials with zero Poisson's ratio for reversible energy absorption applications. Furthermore, thermal testing though heating-cooling

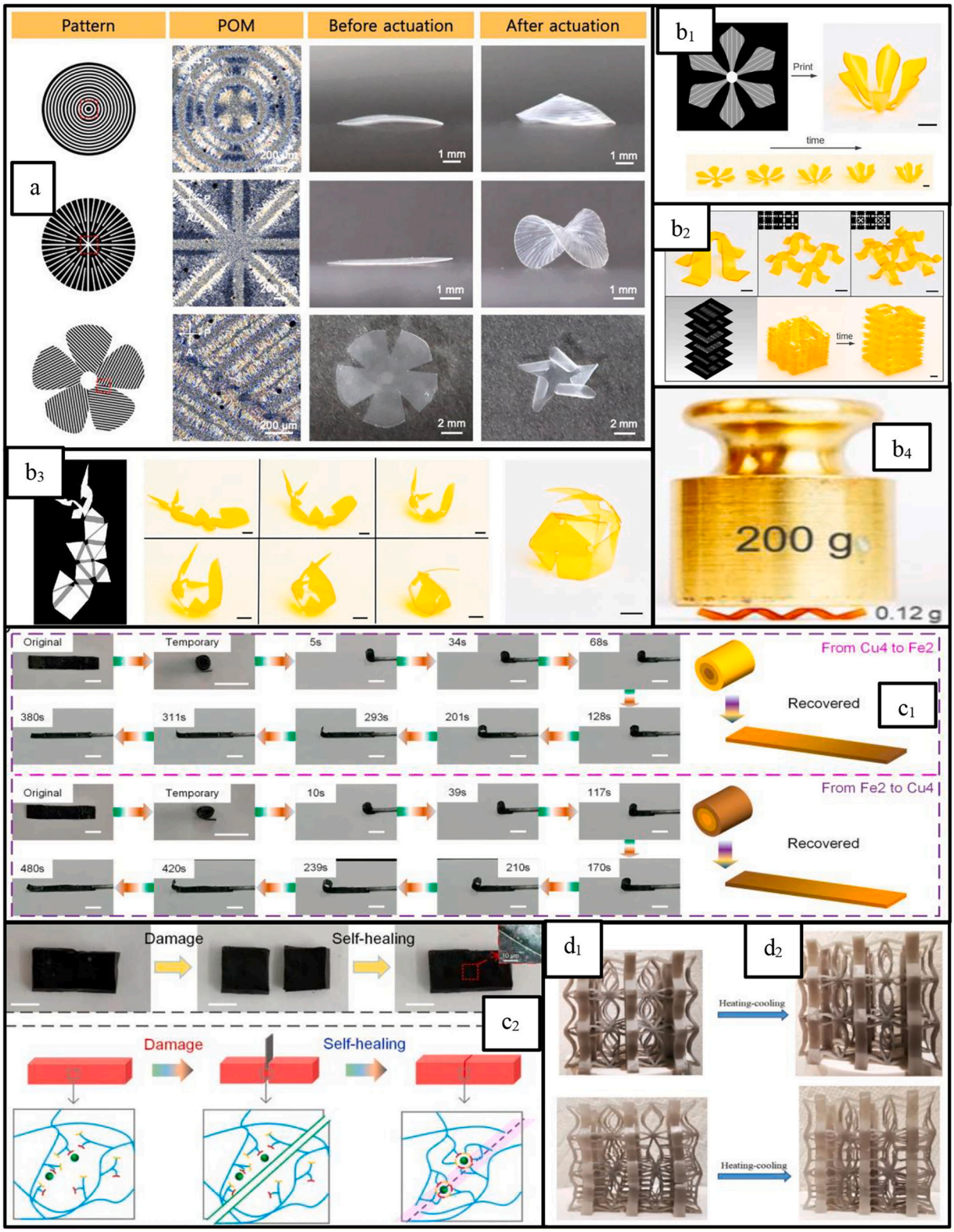


Fig. 12. (a) Different patterns utilized for photoaligning crystal orientation of semicrystalline polymer films, polarizing optical microscope images of photopatterned films, and images of the films before and after thermal actuation in silicone oil at 90 °C (Adapted with permission from ref. [256] Copyright 2021 American Chemical Society); (b_1-b_3) Demonstrations of various complex shape-morphing structures; (b_1) Flower-like structure; (b_2), The two-layer pop-up structure and the multilayer pop-up structure; (b_3) Stanford bunny self-folding; (b_4) Weight holding capacity of 200 g without any obvious cracks (Adapted with permission from ref. [257] Copyright 2020 American Chemical Society); (c_1) Schematic diagram explaining the shape memory mechanism through integration of the metal coordination bonds into PAEK at 130 °C and (c_2) Self-healing performances of PAEK−Cu1and its schematic explanation (Adapted with permission from ref. [258] Copyright 2022 American Chemical Society); (d_1) Before and (d_2) After heating-cooling process on printed metamaterials exhibiting thier shape recovery behavior (Adapted with permission from ref. [259]).

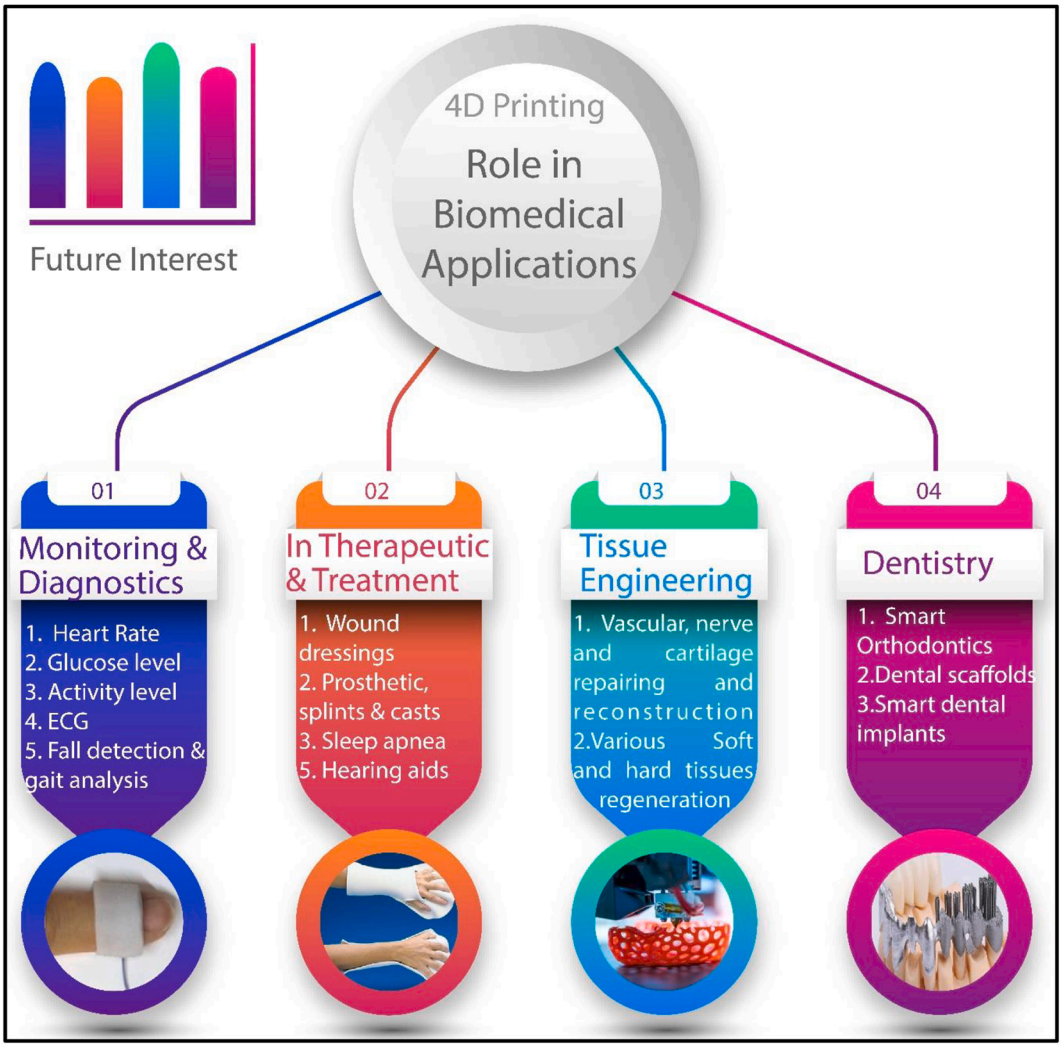


Fig. 13. Potential applications of 4D printing in human parts/organ manufacturing.

process, was performed demonstrating the shape recovery abilities of metamaterials where plastic deformations were fully released and samples attained their original shapes, as presented in Fig. 12(d), for considerable mechanical performances.

3. 4D Printing in biomedical field

4D printing materials should have excellent printability [260]. SMPs are the most important smart biomaterials which are effectively utilized for 4D bioprinting due to their excellent shape memory behavior, biocompatibility, and ease in processing [261–263]. Nowadays, different SMs, including biosensors and actuators were fabricated by researchers for biomedical applications [264–266]. Fig. 13 depicts the most recent 4D bioprinting applications and will be elucidated in this section.

Scaffolds: 4D bioprinting technology is utilized to develop intricate tissues and transform shapes as well as functions of the polymeric materials, which ensure the required cellular stresses [267–269]; thus, this technology is recently exhibited enormous potential for manufacturing scaffolds [270]. Fig. 14(a) illustrates the multiple steps involved in the manufacturing of scaffolds through 4D printing technology, which can help to regenerate traumatized tissue. Porous-structured biodegradable polymer-based scaffolds exhibit excellent in-vivo and in-vitro characteristics for biomedical applications [271–274]. These scaffolds mainly transform their shape but can change their properties, including mechanical properties and electrical properties as well [275]. For instance, Miao et al. [148,276–278] were interested in the investigation of plant-based biopolymers, especially AESO to generate scaffolds with excellent shape memory effect, as illustrated in Fig. 14(b). AESO-based oil polymer exhibited an excellent response to temperature stimulus, and transformed into temporary geometry at −18 °C and recovered to its permanent shape at human body temperature. Additionally, in-vitro analysis revealed excellent proliferation, cell attachment, and functional differentiation of human mesenchymal stromal/stem cells (hMSCs). Similarly, Hendrikson et al. [279] employed PU-based SMP to develop porous scaffolds and modulated cells using mechanical stimulus. The results indicated that scaffold exhibited an excellent shape morphing effect and recovered to its original shape at human body temperature. Thus, these 4D-printed scaffolds can be implanted through minimally invasive procedures.

Similarly, some other biopolymers including lignin and cellulose are highly responsive to humid stimulus [280–283]. For instance, Grigsby et al. [284] developed 4D-printed products by using varying ratios of lignin and keratin. The results showed that lignin/keratin-based filaments can be fabricated at elevated temperatures, which unfortunately, degredation was observed at this temperature. To settle this issue, the paste printing strategies were used, in which hydrogels prepared with 30% - 40% solid content and exhibited excellent properties which ensured their utilization in 4D-printed scaffolds. In another study, Kirillova et al. [285] employed Alg/HA-based biopolymer hydrogels. 4D-

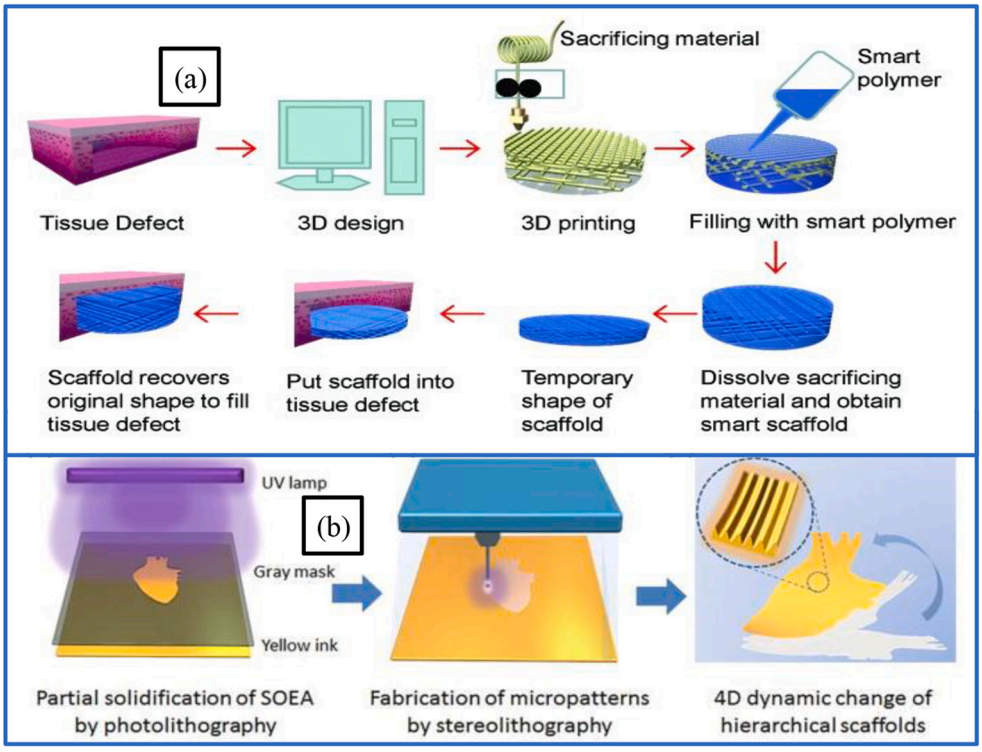


Fig. 14. (a) A schematic illustration of the steps involved for the preparation of 4D-printed scaffolds and its placement in the human cells (Adapted with permission from ref. [278] Copyright 2016, Mary Ann Liebert, Inc); (b) 4D-printed scaffolds for effectively regulating hMSCs cardiomyogenic behaviors (Adapted with permission from ref. [277] Copyright 2018 IOP Publishing Ltd.).

printed self-folding constructs were fabricated by incorporating mouse MSCs, as illustrated in Fig. 15. The results revealed that cells remained undamaged after seven days, thus, depicting excellent biocompatibility. The results of this study also validated that biopolymer-based hydrogels can be applied for manufacturing scaffolds. CS-based biopolymer fabricated with SLA method hydrogel also exhibited excellent shape morphing effects upon temperature stimulus [286], which can be employed to generate scaffolds.

3.1. *Bone tissue engineering/regeneration*

Small bone fractures and defects can be self-repaired. These bone defects have irregular geometries and 4D bioprinting helps the 3D-printed scaffolds to transform their shape upon external stimuli for better bone grating [287–290]. The functionality of polymeric materials developed through 4D bioprinting technology changes with respect to time, which makes it a highly intriguing technology for generating bone grafting scaffolds [230]. Wang et al. [291] constructed photothermal-sensitive β-tricalcium phosphate (TCP) and poly (lactic acid-*co*-trimethylene carbonate) (PLA-TMC)-based scaffolds by adding osteogenic peptide and black phosphorus nanosheets (BPNSs). The results indicated that the shape of the β-TCP/PLA-TMC-based scaffolds was reconfigured through the application of near-infrared radiation (NIR) due to the presence of light-sensitive BPNSs. Additionally, the mechanical characteristics of the scaffolds were comparable to the original trabecular bone at physiological temperature. Furthermore, in-vivo analysis revealed improved bone regeneration through the application of these scaffolds in rat cranial defects.

Another approach to addressing the bone grafting challenge is to swell polymeric materials, which can increase the pore size and consequently help to supply oxygen and nutrients to the internal regions of scaffolds. Gladman et al. [292] incorporated plant-inspired hydrogel composite bio-ink containing acrylamide matrices and cellulose fibrils to generate a dynamic biomimetic 4D-printed structure, as illustrated in Fig. 16(b). Furthermore, this printing strategy aligned cellulose fibrils in one direction that produced swelling deformation in the longitudinal direction. Similarly, Ding et al. [293] fabricated cell-laden scaffold tissues by using polymers including methacrylated alginate (MA), methacrylated gelatin (GelMA), and PEGDA, and ultraviolet (UV) absorber, photo-initiator (PI), and live cells. The study revealed that cell-laden structures exhibited bone-like development of tissues, as depicted in Fig. 16(c).

The in-vivo response of 4D bioprinting is important for fulfilling the global requirements. Several in-vivo studies exist in the literature; for instance, Liu et al. [294] employed HA/PCL-based SMP to fabricate porous scaffolds for implantation in mandibular bone repair for BTE. The results indicated that SMP-based scaffolds compressed into temporary deformed-pore shapes and recovered to porous scaffolds at physiological temperature. Additionally, these smart 4D-printed scaffolds exhibit excellent potential for implantation in dynamic in-vivo conditions.

Su et al. [295] produced NIR light-responsive and peritumoral injectable hydrogel for the remarkable photothermal therapy (PTT) of tongue cancer. These soft material showed excellent biocompatibility and ultra-strong photothermal effect as a result of negatively charged proteins, Ag_3AuS_2 NPs and CS molecules. Results showed that tumors were completely eradicated by one-time PTT treatment during in situ tongue cancer model in mice as presented in Fig. 17(a) with no side effects on surroundings tissues. Thus, potential to use further clinically for the treatment of oral cancers. Wang et al. [296] printed novel MXene-incorporated hollow fibrous (MX-HF) scaffold for promising vascularization and skin flap regeneration due to dynamically responsive behavior triggered by photothermal conversion ability of the MXene nanosheets and temperature-responsive capability of poly (NlPAM) hydrogels in the MX-HF scaffolds. Furthermore, they exhibited a NIR-responsive swelling/shrinkage behavior, which was highly effective for the cell penetration into the scaffold channels from the nearby environment. During in vivo that the NIR-responsive VEGF@MX-

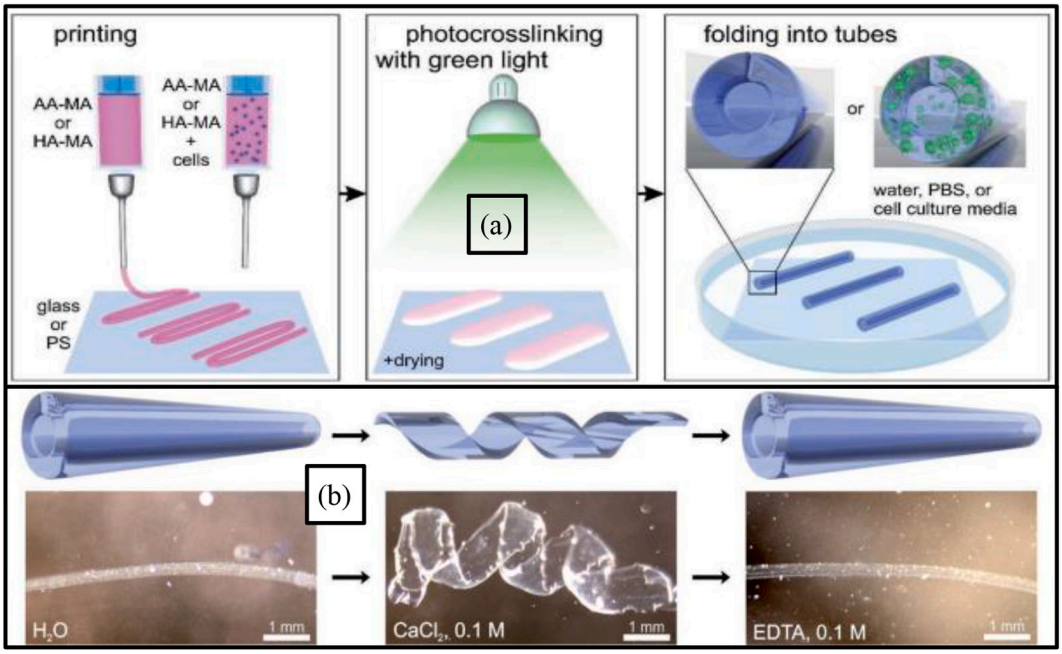


Fig. 15. (a) A schematic illustration depicting the preparation of hydrogel-based cell-laden constructs; (b) MA-based hydrogel depicting the shape-memory effect (Adapted with permission from ref. [285] Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

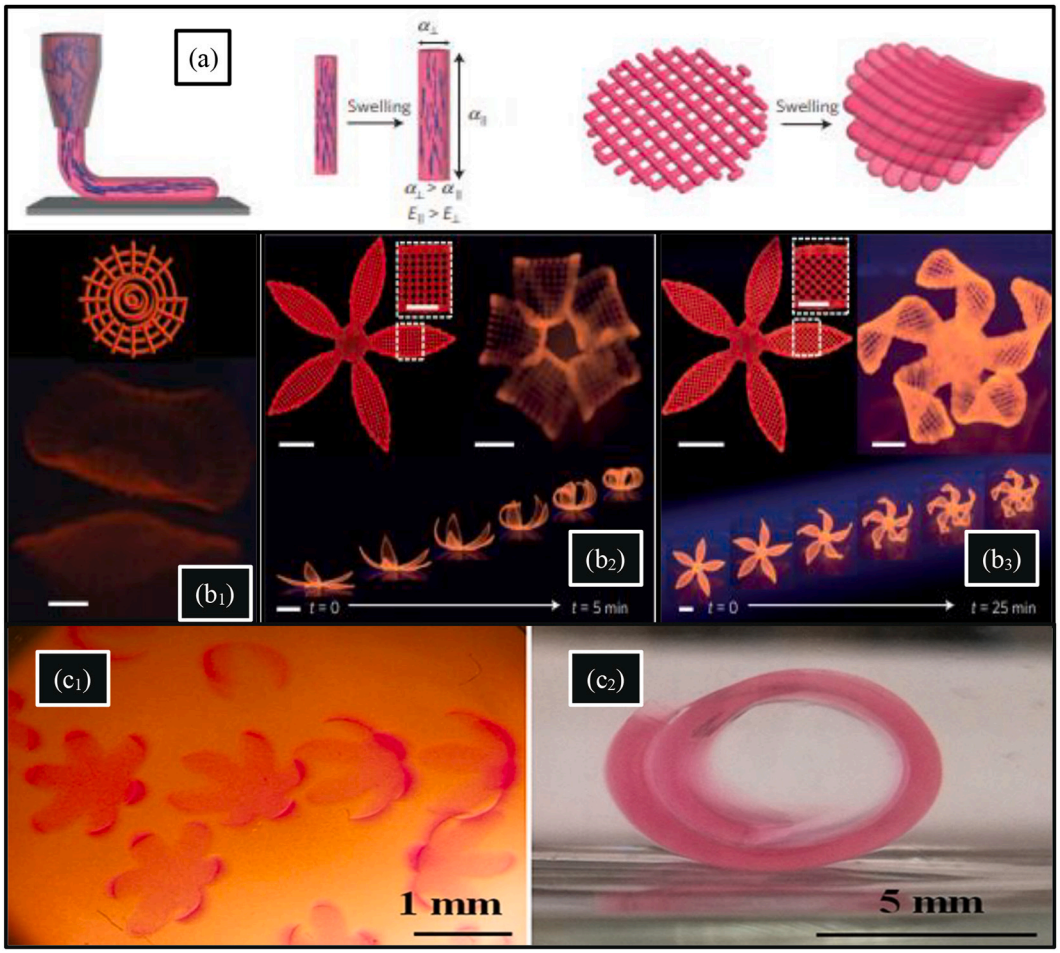


Fig. 16. (a) A schematic illustration of 4D-printed cellulosic fibrils manufactured through DIW and undergoes swelling deformation; (b_1- b_3) 4D-printed self-folding flower which swelled upon water stimulus (Adapted with permission from ref. [292] Copyright 2016, Nature Publishing Group); (c_1- c_2) Bone-like micro-developed 4D-printed tissue fabricated by using stimulus-responsive hydrogel (Adapted with permission from ref. [293]).

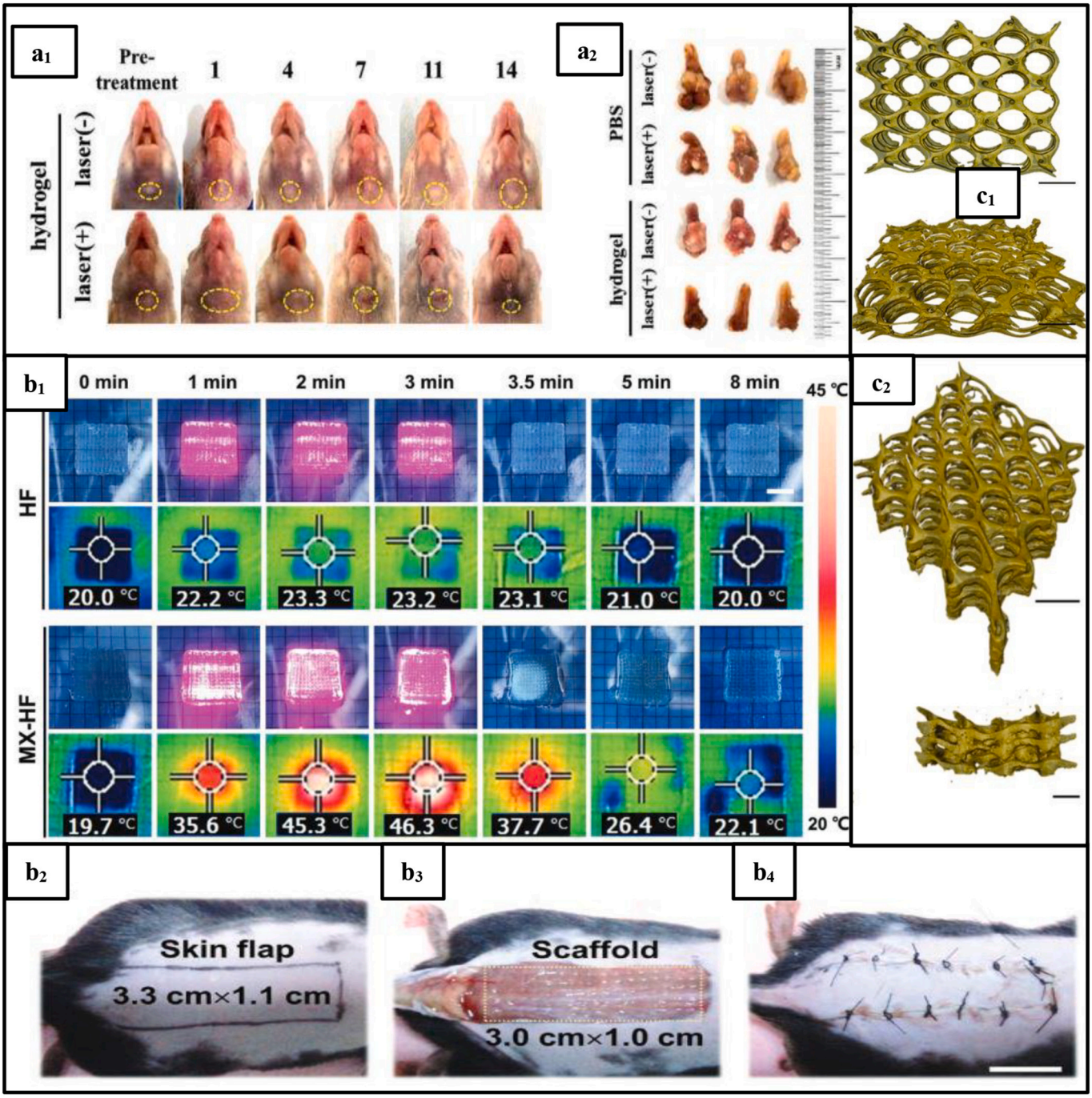


Fig. 17. (a_1) Images of nude mice bearing CAL-27 tumors under four various treatments in 14 days. (a_2) Images of tumor tissues from the mice having four different treatments after the observation for 14 days (Adapted with permission from ref. [295] Copyright 2021 Wiley-VCH GmbH); (b_1) Real-time photographs and thermal images depicting photothermal responsive behavior of the MX-HF scaffolds; (b_2-b_4) In vivo surgical implantation of scaffold in mice (Adapted with permission from ref. [296]); (c_1-c_2) 4D-printed porous scaffolds using thiol−ene "click" chemistry displayed from micro-CT imaging (Adapted with permission from ref. [297] Copyright 2022 American Chemical Society).

HF scaffolds, as presented in Fig. 17(b) effectively enhanced skin flap survival by developing angiogenesis, attenuating apoptosis and decreasing inflammation in skin flaps. Thus, MX-HF scaffolds are helpful for clinical random skin flap regeneration applications. Constant et al. [297] used naturally available terpenes limonene and β-myrcene for developing oligomeric photopolymers for DLP-based 3D printing. Results showed that developed photosets exhibited tunable thermo-mechanical properties and 4D shape memory behaviour. These photopolymers were suitable for scaffold-based biomedical applications, as illustrated in Fig. 17(c).

3.2. Cardiac tissue engineering

4D bioprinting is promising strategy employed to address the challenges related to vascularization tissues and the versatility of this technology has been illustrated through the development of vascularized models of small or large sizes using the self-folding mechanism that transforms 2D-planar geometry to the 3D micro-scaled hollow tubules (MHTs) in response to external stimulus [298], [299]. These models experience localized remodeling through the application of bio-ink material that changes physical characteristics with respect to time

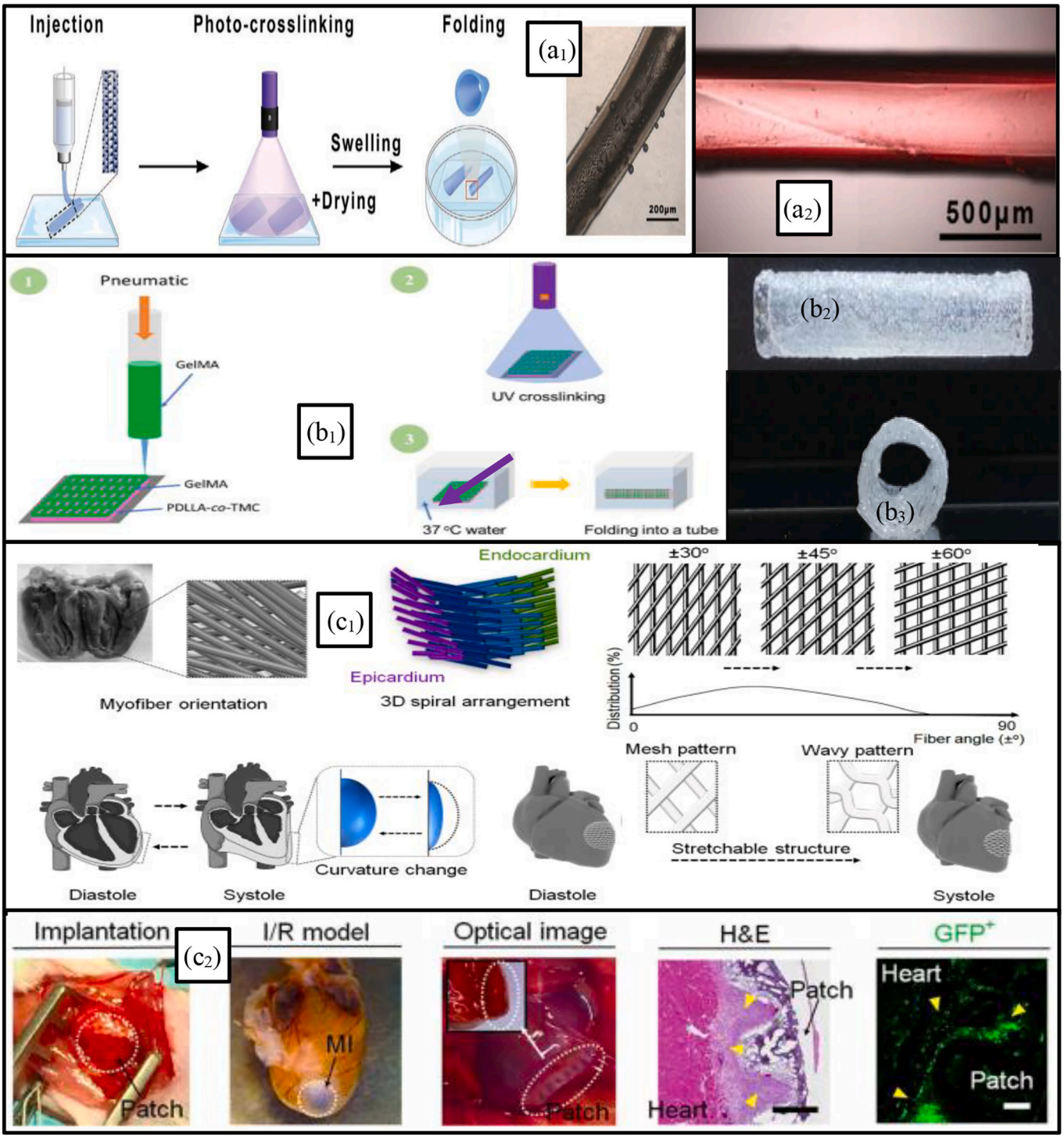


Fig. 18. (a_1) A schematic diagram illustrating the steps involved for the fabricated of GelMA-based MHTs; (a_2) Morphology of MHT (Adapted with permission from ref. [303]); (b_1) A schematic illustration of 4D printing for manufacturing of GelMA/PDLLA-co-TMC-based microvascular scaffolds; (b_2-b_3) Macro-photographs of GelMA/PDLLA-co-TMC-based scaffolds (Adapted with permission from ref. [304] Copyright 2020, The Materials Research Society); (c_1) Figure depicting the design of BCP which is manufactured through 4D printing technology and by inclined fiber angles (30^o, 45^o & 60^o) which provide better curvature and stretchability; (c_2) In-vivo response of the 4D-printed patch (Adapted with permission from ref. [306] Copyright 2020, Science Advances).

[300] Contrary to 3D bioprinting, 4D-bioprinting also helps to achieve homogeneous cell distribution in MHTs [301]. Nowadays, SMPs, photo cross-linkable hydrogels and MSCs are primarily applied to develop self-folding architectures through 4D bioprinting [302]. Additionally, photo cross-linkable hydrogels can be self-folded for constructing microvascular scaffolds through water stimulus [303], as illustrated in Fig. 18(a). Similarly, Lai et al. [304] 4D-bioprinted GelMA/poly(d,l-Lactic Acid) (PDLLA)-*co*-TMC-based scaffolds by regulating the degree of orientation, as depicted in Fig. 18(b). The developed microvascular scaffolds folded upon heating at physiological temperature and possessed internal diameters comparable to the blood vessels. Additionally, these MHTs exhibited extraordinary biocompatibility and cell proliferation. Furthermore, extrusion-based bioprinting technologies have also been utilized for developing bilayer MHTs of melt electro-writing of polymer

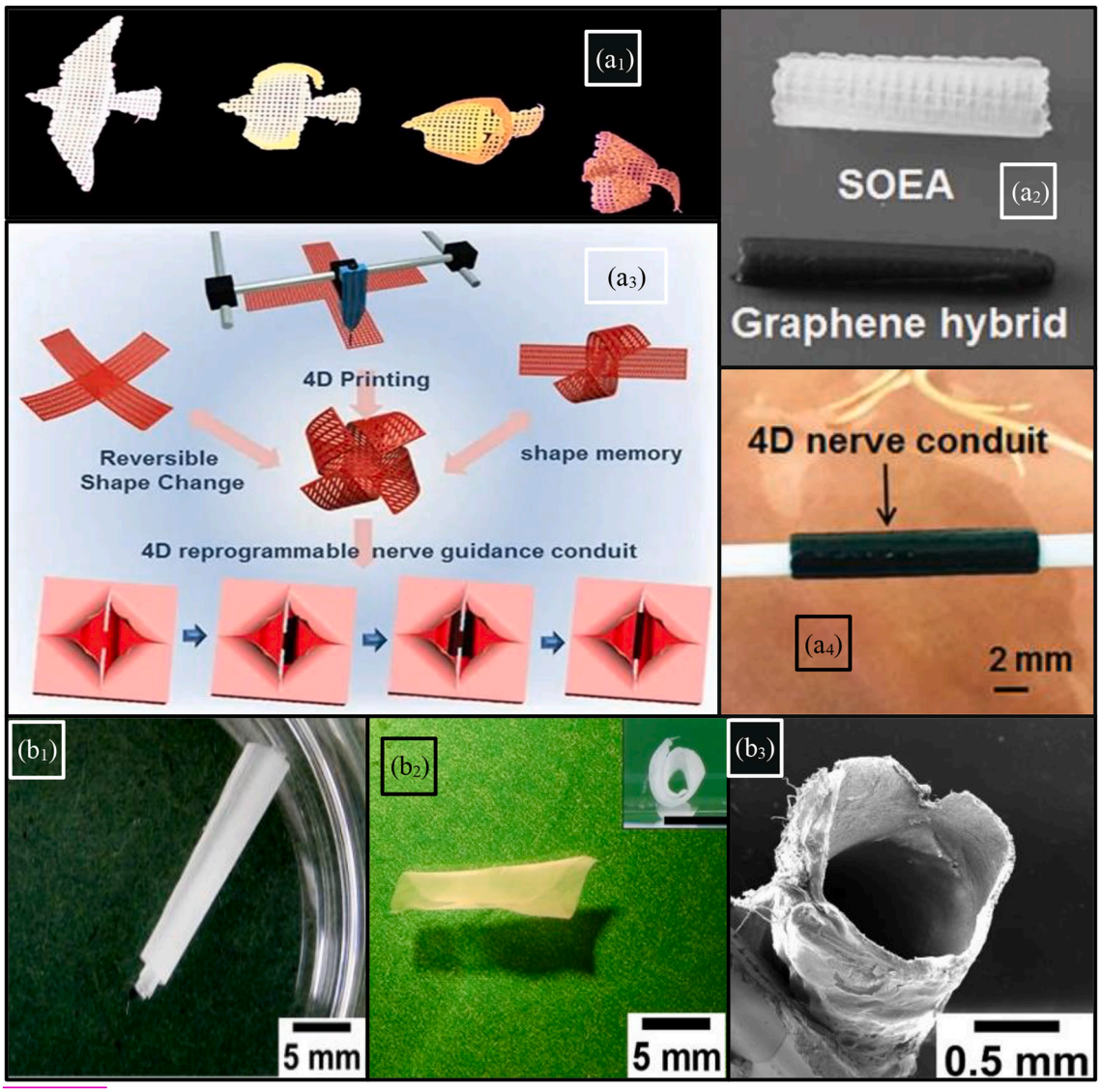


Fig. 19. 4D-printed graphene nanohybrid based reprogrammable NGC; (a_1) Different models of bird flying architectures; (a_2) Actual 4D-printed reprogrammable NGC; (a_3–a_4) Design of the full entubulariation of 4D NGC via a "thermomechanical programming" shape transformation, (Adapted with permission from ref. [174] Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (b_1) Macro-image showing self-folded PGS-PCL/MA-HA bilayer before degradation; (b_2) Macro-image showing self-folded PGS-PCL/MA-HA bilayer after 1 month of degradation; (b_3) SEM image of PGS-PCL/MA-HA bilayer (Adapted with permission from ref. [311]).

composites and photo cross-linkable hydrogels [305]. 4D printing of vascular models is still in its rudimentary phase. There is a need to address different challenges, including reversible spatio-temporal control of the stimuli-responsive strain of 4D-printed constructs as well as cellular orientation in vascular systems.

Hydrogel-based 4D-printed cardiac scaffolds for myocardial repair were constructed by Luo et al. [237] through polydopamine (PDA)/Alg and cell-laden hydrogel triggered through NIR. The results indicated that these scaffolds exhibited high viability after two weeks of cell culture by maintaining their deformed architectures. Similarly, Cui et al. [306] developed an adaptable GelMA/PEDGA-based bioengineered cardiac patch (BCP) by using SLA technology and seeded through human endothelial cells (hECs), hMSCs, and human-induced pluripotent stem cell–derived cardiomyocytes (hiPSC-CMs) for fabricating cellular patch. Moreover, myofibrils were also employed at different orientations to treat myocardial infarction (MI), as illustrated in Fig. 18(c). The in-vivo results indicated that the cellular 4D-printed patch exhibited improved biocompatibility, blood density, and attachment with the heart. Serpooshan et al. [307] constructed hiPSC-CMs-based tissues by using acoustic stimuli. These printed tissues possessed better cardiac functions, including beat frequency, contractile stress, and relaxation-contraction rates. This intriguing development could provide a breakthrough for 4D bioprinting, in the future.

Contrary to these polymers, AESO-based plant-derived polymer has also been employed by Miao et al. [277] and observed excellent biomechanical performance and attachment with traumatized tissues of cardiac. Similarly, MSCs along with methacrylate, HA, and Alg-based hydrogels are utilized for developing 4D-printed MHTs which can be applied as blood vessels [308]. Although, 4D bioprinting technology is investigated for cardiac TE applications, however, there is still a need to develop novel bio-ink materials as well as cellular patterning. By addressing these challenges, 4D-bioprinted cardiac components may be applied for treating patients suffering from cardiovascular diseases.

3.3. *Neural tissue engineering*

Neural tissue engineering (NTE) scaffolds can mimic the structure and composition of ECM to assist cellular adhesion, proliferation, and

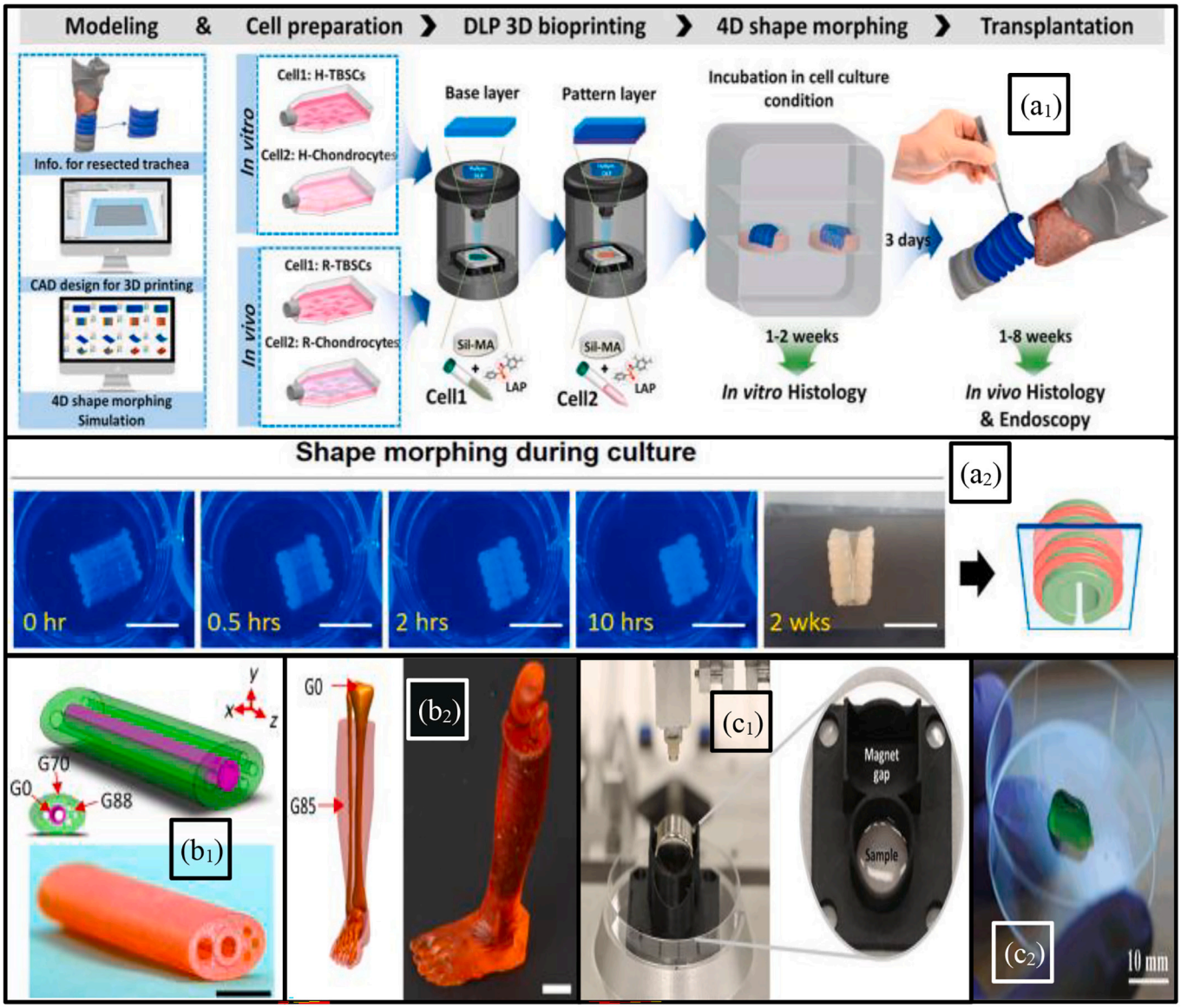


Fig. 20. (a_1) A schematic illustration showing the step involved in the fabrication of silk fibroin-based 4D-printed hydrogel; (a_2) Figures depicting the shape morphing effect which is achieved through in-vitro culture (Adapted with permission from ref. [317] Copyright 2020, Elsevier); (b_1-b_2) Different views showing the design of the artificial limb structure with mixture of hard and soft muscles (Adapted with permission from ref. [318]) (c_1) 4D-bioprinted adapter which incorporates magnetic forces for remodeling of bio-ink materials; (c_2) 4D-printed polymer-based artificial cartilage (Adapted with permission from ref. [319] Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

differentiation [309]. Additionally, 4D-printed micro-grooves also help nerves to grow in specific directions, as nerve function depends upon the reconnection of the nerve fibers [310]. The NTE approach has been employed by Miao et al. [174] to develop nerve guide conduits (NGCs) through 4D bioprinting and by using bio-ink containing AESO, hMSCs, and graphene, as depicted in Fig. 19(a). Photo-sensitive AESO-based polymer induced bending in the printed structure, whereas, graphene-based NPs enhanced the conductivity of the biomaterial by promoting hMSCs differentiation into neural cells. The authors noted that AESO-based SMP recovered their permanent shape at 37 °C and this characteristic was applied to develop smart NGCs which exhibited multi-functional properties for nerve grafting including dynamic entubulation, chemical cues, physical guidance, and seamless integration.

Thermo-sensitive PU-based hydrogel exhibits improvement in stiffness properties without incorporating any crosslinker [312]. Hsieh et al. [313] dispersed neural stem cells (NSCs) into PU-based hydrogel before the incorporation of gelatin. The results indicated that printed bioproducts exhibited extraordinary proliferation and differentiation at physiological temperature. The in-vivo response of biodegradable hydrogel in a zebrafish model revealed that 4D-printed products successfully rescue zebrafish from nerve injury. Likewise, Apsite et al. [311] developed NGCs using poly(glycerol sebacate) (PGS)-PCL/MA-HA-based bilayer mats. The results indicated that printed soft NGCs exhibited excellent biocompatibility and degradation resistance, as illustrated in Fig. 19(b). Additionally, neuron cells (PC-12) cultured on artificial nerve grafts also displayed excellent cellular adhesion, differentiation, and proliferation. Similarly, Wu et al. [314] also fabricated a self-healing hydrogel through 4D bioprinting that could potentially be applied for nerve regeneration.

3.4. Cartilage tissue engineering

4D bioprinting technology develops appropriate cartilage tissue engineering (CTE) scaffolds to regenerate cartilage tissues at the damage

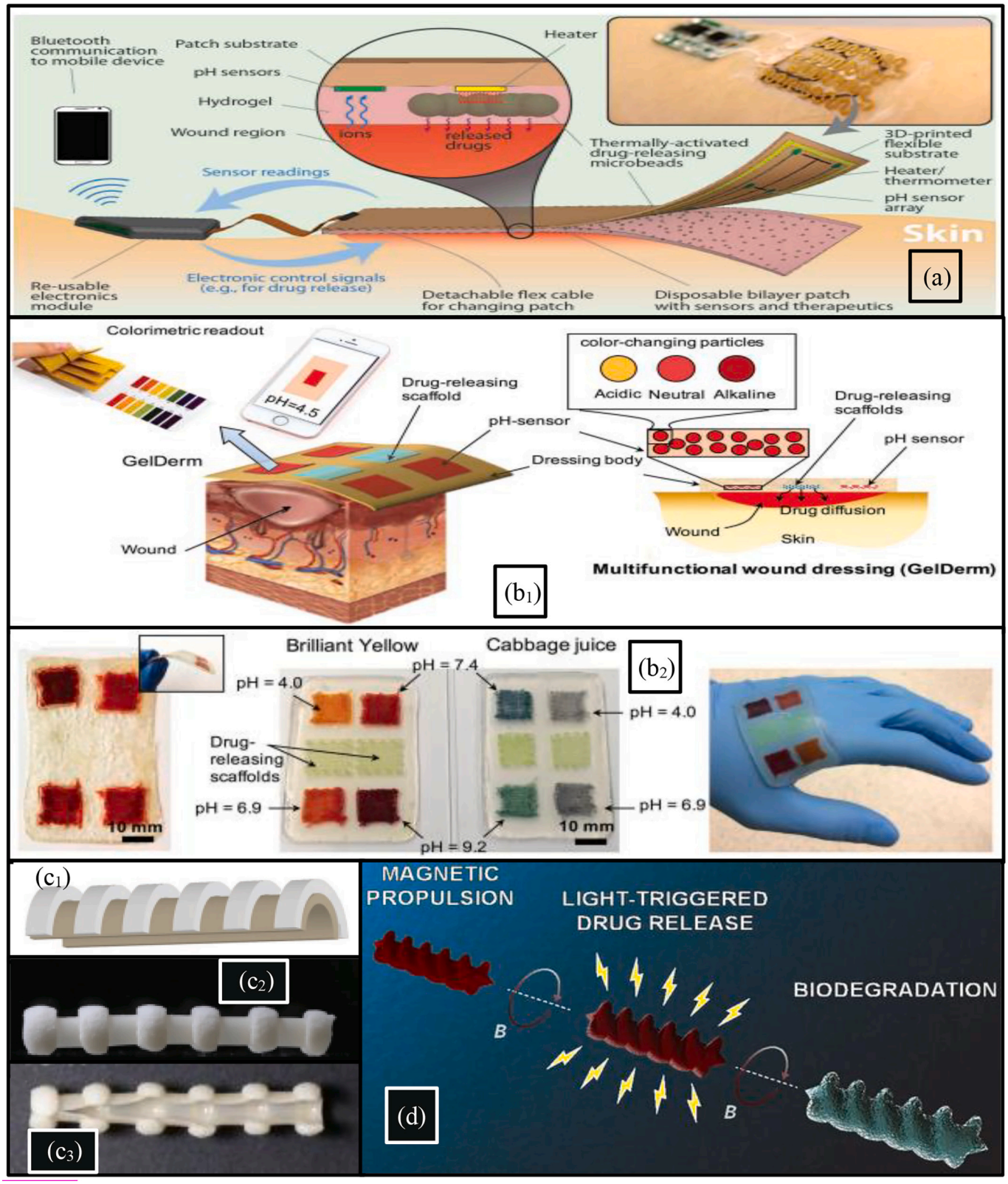


Fig. 21. (a) Smart automated bandage containing pH-sensitive sensors which are capable of releasing drugs upon thermo-responsive stimulus (Adapted with permission from ref. [240] Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (b_1) A schematic illustration of pH-responsive GelDerm dressing for epidermal injury; (b_2) 4D-printed pH-sensitive sensor model that detects pH variation at the injury location. Drug-eluting scaffolds deliver antibiotics at the traumatized tissues to kill bacteria (Adapted with permission from ref. [232] Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (c_1-c_3) Biomolecule-responsive 4D-printed hydrogel-based drug delivery tube (Adapted with permission from ref. [324] Copyright 2022, Wiley-VCH Gmbh); (d) Light-responsive CS-based helical micro-swimmer for targeted drug delivery (Adapted with permission from ref. [328] Copyright 2018 American Chemical Society).

locations [315]. 4D bioprinting technology has also been employed to develop curved-trachea implants for cartilage repair [316]. For instance, uni-aligned nanocellulose fibrils embedded in acrylamide matrices produce longitudinal deformation upon swelling. Intricate curvatures are filled after the swelling process [292]. For instance, Kim et al. [317] 4D-printed trachea implant through photo-crosslinked silk fibroin-based hydrogel, as illustrated in Fig. 20(a). The authors employed DLP technology to manufacture a cell-laden hydrogel structure, which was implanted into rabbits to evaluate its in-vivo response. The results revealed that excellent cartilage regeneration was observed in the rabbit trachea.

By considering CTE applications, Betsch et al. [319] controlled the direction of collagen fibers through the real-time remodeling of the matrix during the printing and employed this approach to develop artificial fibrocartilage. The authors were managed to develop complex cartilage scaffolds containing different layers of magnetic chondrocyte-loaded bio-ink, as illustrated in Fig. 20(c). Some structures, including fish-scale and tendon-bone attachment, exhibit heterogeneous composition and different characteristics [320]. Kuang et al. [318] developed 4D-printed functionally-graded polymeric products with tailorable mechanical characteristics. The authors reported that soft muscles around the bones as depicted in Figure 20(b) can be printed through these materials.

3.5. Drug delivery systems

A wide range of DDSs including tablets, multilayered DDSs, transdermal systems, orodispersible films, dermal skin patches, nanosuspensions, rectal and vaginal delivery systems can be generated with ultra-high accuracy by using 4D bioprinting technology [321–323]. 4D bioprinting not only tailors the mechanical strength or shape, but it helps to deliver bio-molecules by responding to external signals [324–326]. The interest in stimuli-responsive DDS has been continuously developing owing to the better control of the drug delivery profiles [327]. Recently, smart automated bandages have been developed containing pH-sensitive sensors which are capable of releasing drugs upon external responses, specific signals, and abnormal pathological states [240], as illustrated in Fig. 21(a).

The integration of stimulus-dependent response in 4D-bioprinted DDS to control drug release [51]. For instance, Malachowski et al. [329] fabricated thermo-responsive PNIPAM-AAc/poly(propylene fumarate) (PPF)-based DDS which released drugs in a controlled fashion for treating the gastrointestinal tract. 4D-printed helical micro-swimmers for targeted DDS have also been developed by adding MNPs into the photocurable resins. In another study, Bozuyuk et al. [328] developed a CS-based helical micro-swimmer that was triggered by UV light, as illustrated in Fig. 21(d). The results indicated that the developed micro-swimmer exhibited excellent biodegradability and drug-releasing ability. Similarly, Gupta et al. [330] developed a 4D-printed capsule exhibiting a core-shell hydrogel system that could release the drugs on-demand at specific locations. The core part of the capsule contained ethylene glycol, poly(vinyl alcohol), and bio-molecules, whereas the shell contained gold nanorods (AuNRs) and poly(lactic-co-glycolic acid) (PLGA). These photo-responsive AuNRs ruptured and released drugs in response to laser stimulus.

Ma et al. [331] developed PLA/PCL-based composites with an outstanding shape memory effect under the heating stimulus. The PLA/PCL-based composites demonstrated excellent shape recovery/shape fixation rates were above 92%. Furthermore, a drug release device was fabricated based on these composites to simulate sequential petal opening and sequential drug releasing effects, respectively, as presented in Fig. 22(a). Likewise, Lee et al. [332] developed multistimuli-responsive triblock copolypeptides made from thermosensitive elastin-based polypeptides (EBP) and ligand-responsive calmodulin. Under identical conditions the concentrated ECE triblock copolypeptides demonstrated thermally induced gelation, which results in physically crosslinked hydrogels. These hydrogels exhibited controlled mechanical and rheological characteristics based on the conformational change of the calmodulin middle block due to binding either Ca^{2+} or Ca^{2+} and trifluoperazines ligands, as presented in Fig. 22(b), and also exhibited strong biocompatibility. The ECE triblock hydrogels with stimuli responsiveness can be served as injectable drug delivery depots for biomedical applications. Xin et al. [333] developed pH-responsive hydrogel-based environmentally adaptive shape-morphing microrobots (SMMRs). The fabricated SMMRs were programmatically encoded with various expansion rates. A shape-morphing microfish (SMMF) was also designed to encapsulate a drug doxorubicin (DOX) through closing and opening of its mouth in phosphate-buffered saline (PBS), (pH $\sim$ 7.4) and in a slightly acidic solution (pH $<$ 7) condition respectively. Furthermore, localized human cervical cancer cells (HeLa) cell treatment through an artificial vascular network was performed by "opening−closing" of the SMMF mouth, as presented in Fig. 22(c). Thus, highly effective for various applications such as on-demand drug release and complex microcargo operations.

Chen et al. [334] proposed a magneto-active-based millirobot with ability to transform freely and rapidly from solid−liquid state under weak magnetic field (~0 mT) and the bingham plasticity in the solid state upon a strong magnetic field (~100 mT) using a magneto-rheological fluid (MRF). The developed MRF robot capable to perform various functions-based on its state for example in the liquid state it offered diverse behaviors of large deformation, in situ splitting, smooth navigation, merging, and gradient pulling triggered by a weak magnetic field having high gradient and in the solid state it offered controllable locomotion with reconfigured shapes and wide range of object manipulations (including push, pull and rotate the objects) triggered by a strong magnetic field having a high gradient. A case study based on the its various diverse tasks accomplishment of MRF-Robot, is elaborated in Fig. 23 depicting the complete liquid-drug delivery, thrombus clearance, and fluid-flow restriction in the phantom vascular model under magnetic actuation.

3.6. Medical devices

4D bioprinting has enabled the world to develop intricate and patient-specific medical devices, including vascular repairing devices, stents, and orthopedic implants [335]. Recently, SMP-based drug-eluting stents have been utilized by the medical field for precisely controlling the drug release. These stents are also primarily utilized for vascularization [336]. These stents not only open blood vessels but also help to release antiplatelet and antiproliferative drugs [223]. Invasiveness in surgeries can also be minimized through 4D-printed stents. Thermo-responsive and chemo-triggered polymeric materials are usually used for the fabrication of helical products, as these products exhibit extraordinary biomechanical resistance [337]. Additionally, other factors including release performance, biocompatibility, adhesion with platelets are also considered important.

Wang et al. [338] studied shape-programmable 3D microfluidic structures-based on a bilayer of channel-embedded PDMS and SMPs, particularly for diverse geometries such as in open-mesh configurations. A wide range of 3D structures for microfluidic devices were developed, as presented in Fig. 24(I). Reverse shape morphing behavior and programming was observed under temperature stimuli. Fluid flow in the microfluidic channels maintained well in both deformed and recovered shapes. Furthermore, fast actuation of 3D microfluidic structures was also observed as a result of adding of magnetic particles into the PDMS layer, and later controlled via a portable magnet. Thus, developed open-mesh 3D microfluidic structures having complete shape-programmable behavior highly effective for drug delivery, and tissue engineering-based many biomedical applications. In another study, Wang et al. [339] developed functional biorobots composed of live cardiomyocytes under tunable acoustic fields. These biorobots performed actuation functions through both naturally occurring contraction-relaxation

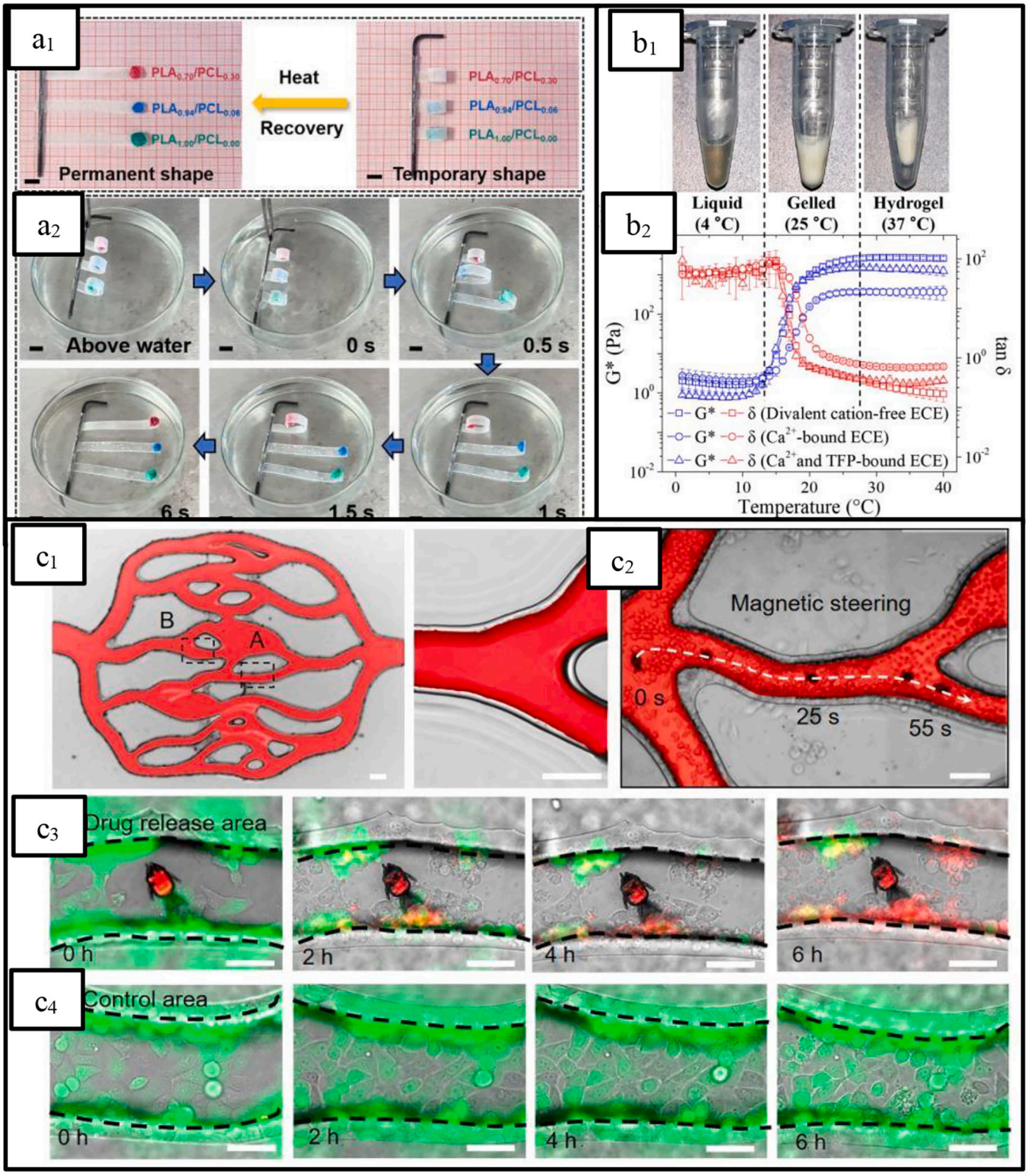


Fig. 22. (a_1) PLA/PCL-based composites for drug release device having different pellets. The images showing the device with "released" permanent state and "closed" temporary state; (a_2) The sequential drug release pattern of the various pellets under different times (Adapted with permission from ref. [331] Copyright 2021, Zhejiang University Press, part of Springer Nature); (b_1) Images of the temperature-dependent gelation of divalent cation-free ECE triblock copolypeptides; (b_2) Rheological characteristics of ECE triblock copolypeptide solutions based on temperature trigger and conformational change of the calmodulin block upon ligand binding (Adapted with permission from ref. [332] Copyright 2022 American Chemical Society); (c_1) Artificial networks due to photolithography and PDMS molding; (c_2) Magnetic SMMF swimming in the networks; (c_3) Images of the viability of HeLa cells in the DOX-releasing area (A in (c_1); (c_4) Images of the viability of HeLa cells in the control area (B in (c_1)) (Adapted with permission from ref. [333] Copyright 2021 American Chemical Society).

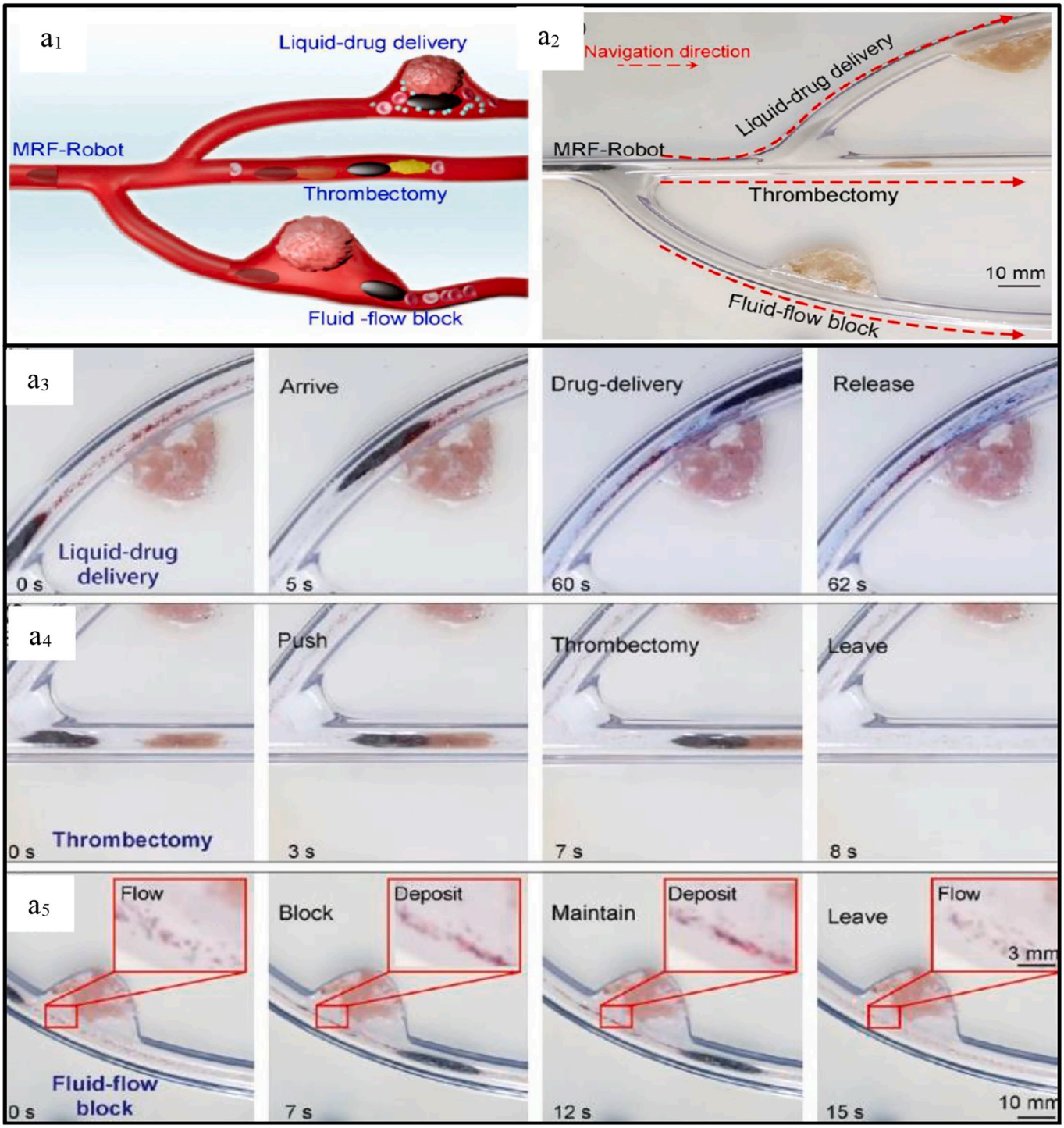


Fig. 23. (a_1) Schematic depiction of cardiovascular disease treatment with the MRF-Robot; (a_2) 3D printed phantom vascular model. MRF-Robot navigated in the phantom vascular model and performed various functionalities, such as (a_3) On-demand liquid-drug delivery; (a_4) Active thrombus clear, and (a_5) Effective fluid-flow block (Adapted with permission from ref. [334] Copyright 2022 American Chemical Society).

cycles and external control with chemical and electrical stimuli such as controlled actuation of a soft skeleton and pumping of microparticles, as presented in Fig. 24(II). Cui et al. [340] introduced dynamic thiocarbamate bonds into the photocurable methacrylate for the development of reprocessable and self-healable polythiourethane (PTU)-based different objects. The shape memorized PTU demonstrated excellent shape fixity, shape recovery, the surface wettability, and excellent biocompatibility through printing of a hand model, as presented in Fig. 24(III). 4D-printed PTU possessed wide range of applications particularly for of bio-implants.

The influence of biodegradability on the mechanical characteristics of stents is also taken into consideration while developing the microstents [341]. Most stents are employed to expand the trachea or blood vessels, and recently, some researchers fabricated high-resolution SMP-based thermo-responsive cardiovascular stents through 4D printing technology. Cabrera et al. [342] fabricated a polymer-based cardiovascular stent through FDM technology. The results indicated that the developed stent transformed into pre-design geometry at 37 °C, and

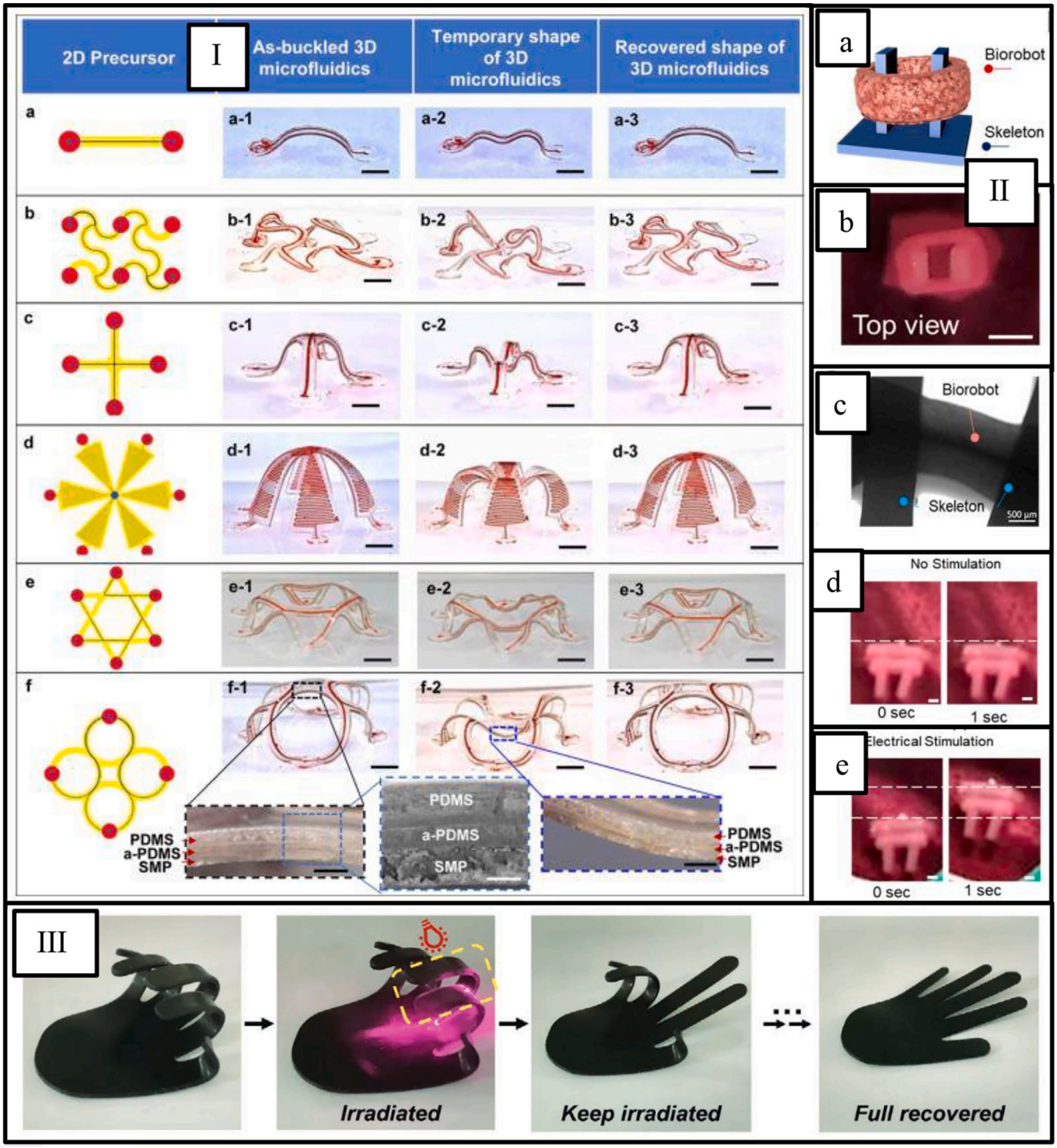


Fig. 24. (I) Shape-memory behavior of 3D microfluidic configuration-based various structures/shapes (Diluted red food dye injected into microfluidic channels for demonstration); (a) "Ribbon" structure; (b) "Stadium" structure; (c) "Table" structure; (d) "Umbrella" structure; (e) "Basket" structure; (f) "Box" structure, with optical and SEM images of the cross section of the SMP/PDMS interface; (a – f) buckled structures all was in 3 mm where as 250, 100, and 250 μm scale bar from left to right (Adapted with permission from ref. [338] Copyright 2022 American Chemical Society); (II) (a) Scheme diagram of biohybrid actuator comprising of ring biorobot and PU soft skeleton; (b) Top view of biohybrid actuator; (c) The ring surrounding the soft legs of the skeleton through microscopic image; (d) Biohybrid actuator in absence of electrical stimulation; (e) The same actuator with electrical stimulation presenting displacement. (a-e) The scale bar is 1 mm (Adapted with permission from ref. [339] Copyright 2022 American Chemical Society); (III) Shape memory behavior of 4D-printed PTU/CNTs-based hand model (Adapted with permission from ref. [340] Copyright 2022 Wiley-VCH GmbH). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

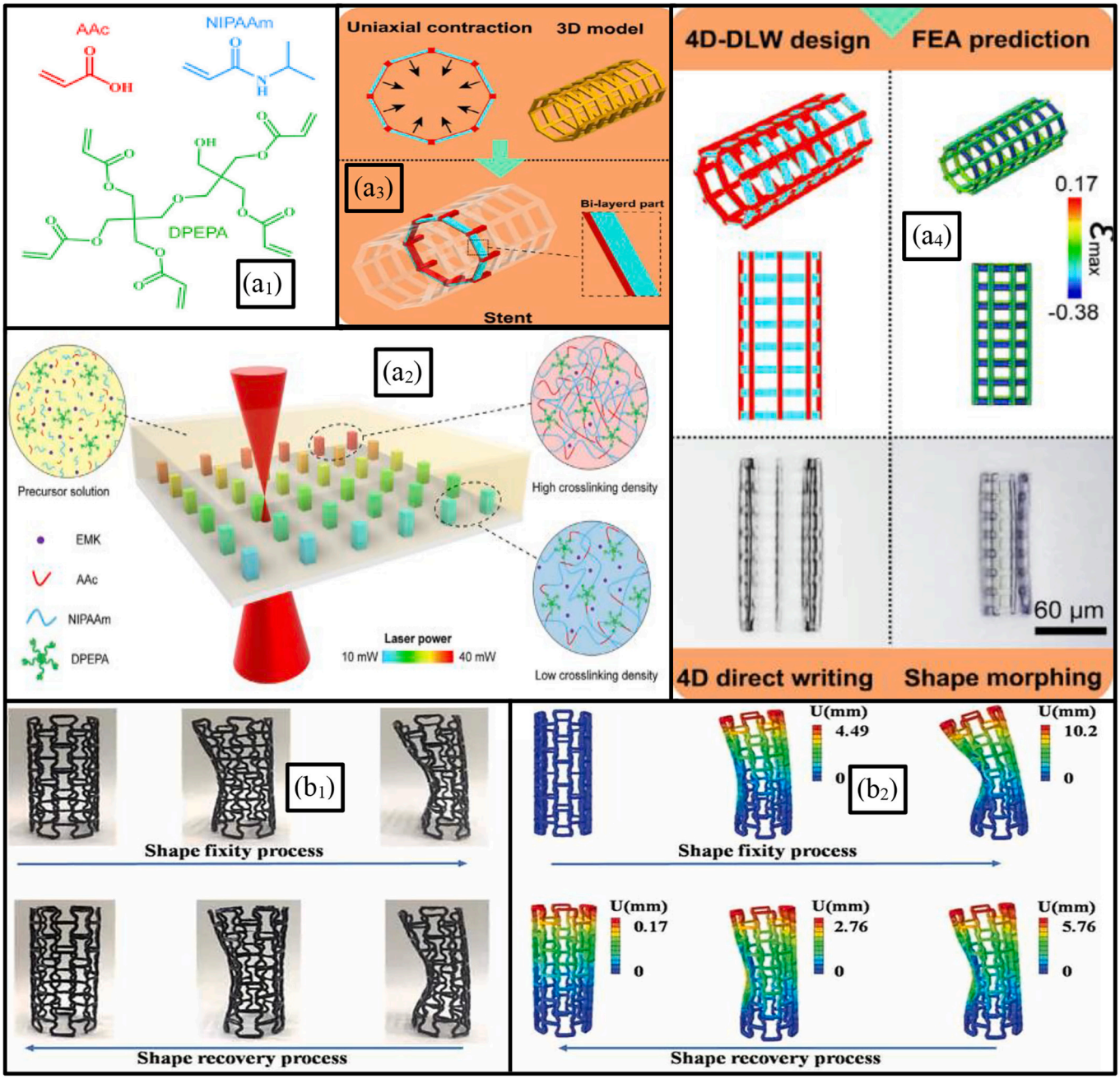


Fig. 25. (a_1) Schematics of polymers employed for fabricating stent; (a_2) A schematic illustration of DLW technology in which hydrogel-based 4D-printed product was developed with increased cross-linking density by increasing the power; (a_3-a_4) Figures depicting the designing of 3D reconfigurable stents and sophisticated design parameters were adjusted through FEM (Adapted with permission from ref. [343]); (b_1- b_2) Shape recovery behavior of 4D-bioprinted PLA/Fe_3O_4-based SMPC tracheal stent (b_2) showing FEM simulation of stents (Adapted with permission from ref. [202]).

crack appeared upon degradation. However, there is further need to explore in-vivo response. Similarly, Jin et al. [343] developed PNIPAM-AAc/dipentaerythritol pentaacrylate (DPEPA)-based sophisticated stent using DIW technology. The finite element method (FEM) was employed for the adjustment of design by assessing the stimuli response, as illustrated in Fig. 25(a). The results indicated that the developed 4D-printed stent was thermo- and pH-responsive. Additionally, stimuli-response and material stiffness were strongly linked with each other. These systems can be employed to manufacture products for dynamic working environments.

The tracheal-bronchial stent is a hollow tube that is employed to expand the human airways and help breathe [344]. Conventional trachea stents exhibit a static nature under continuous fatigue load caused by breathing. Therefore, 4D bioprinting technology has been utilized to develop stimuli-responsive stress-free customized stents [345]. By sensing the surrounding situation, 4D-printed morphing stents adjust for dynamic stresses triggered by body temperature. Zarek et al. [241] developed 4D-printed biodegradable PCL-based SMPs tracheal stents by using SLA technology. The in-vivo results indicated that the 4D-bioprinted tracheal stent modified their configuration in a dynamic

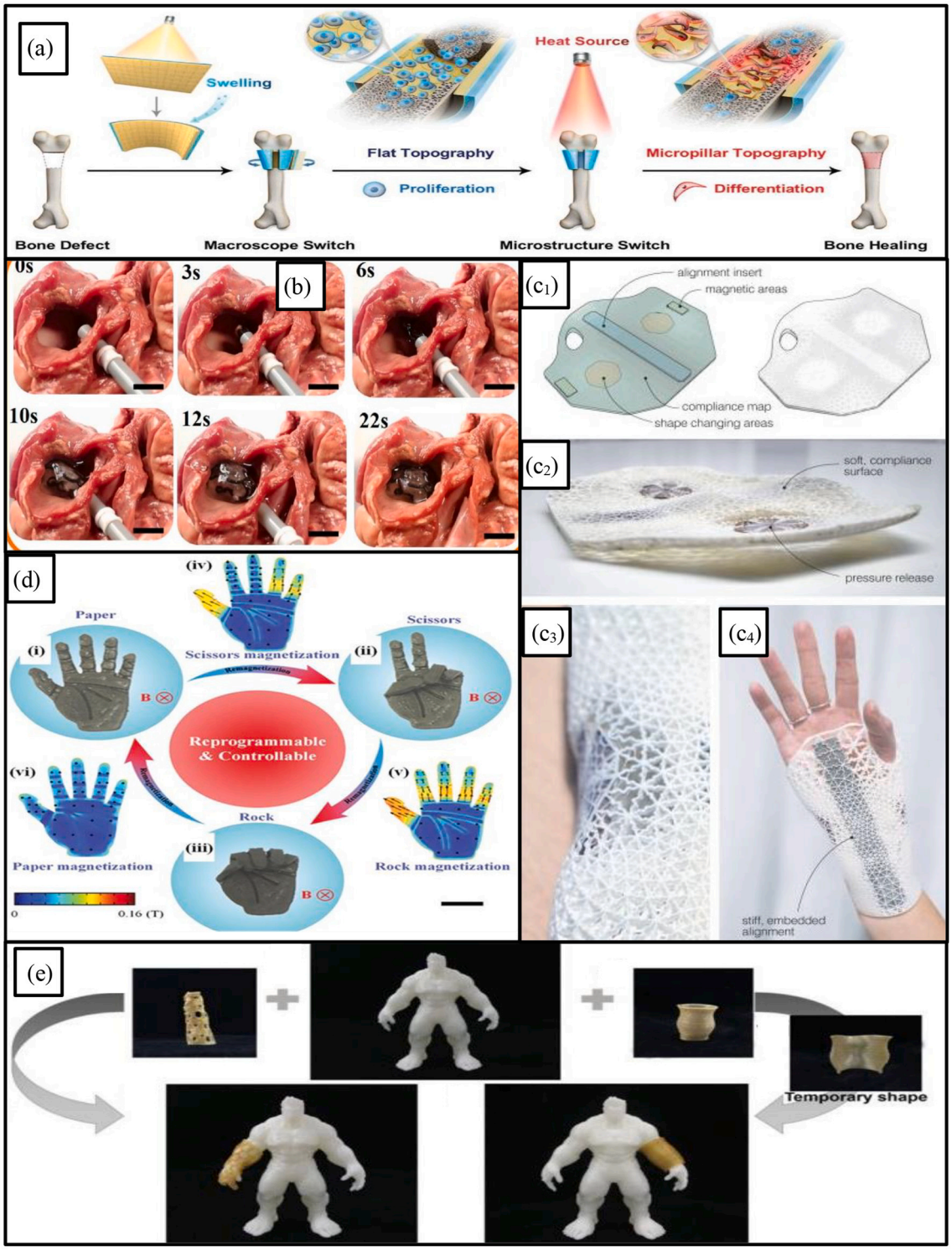


Fig. 26. Examples of 4D-printed parts in biomedical applications; (a) 4D-printed bilayer membrane for bone repair (Adapted with permission from ref. [243] Copyright 2021, Wiley-VCH Gmbh); (b) In-vitro feasibility study of transcatheter LAA closure (Adapted with permission from ref. [229] Copyright 2021 American Chemical Society) (c_1) Actual design model of a multipurpose orthotic splint; (c_2) Pressure release and the distribution of hard and soft areas of the 4D-printed splint; (c_3) Features of the 4D-printed mesostructured; (c_4) Orthotic splint as worn by the user (Adapted with permission from ref. [349]); (d) Bionic hand transformations from paper gesture into different gestures; (a) paper; (b) scissors; (c) rock (Adapted with permission from ref. [350] Copyright 2021 American Chemical Society); (e) 4D-printed PLA/PCL-based filaments for elbow protectors in adaptable and personalized mode (Adapted with permission from ref. [226] Copyright 2020, Elsevier).

microenvironment. Similarly, Zhang et al. [202] fabricated a 4D-printed Fe_3O_4/PLA-based tracheal stent which exhibited extraordinary shape memory behavior upon magnetic stimulus and UV light, as illustrated in Fig. 25 (b). This stent also exhibited minimal volume and invasive injury. 4D bioprinting technology has shown that it can be used to make artificial scaffolds for intravascular and tracheal stents.

3.7. Other biomedical applications

4D bioprinting is a propitious technology that possesses excellent potential to develop other 4D-printed products [346]. Fig. 26 shows other biomedical applications, including the development of bionic hands, splints, and elbow protectors. In another novel work, Kashyap et al. [347] proposed the radioscopic examination of the 4D-printed porous PU-based SMP. The addition of sodium chloride salt and tungsten developed porosity and radiopacity, respectively. These developed foams were cleaned with distilled water, thus yielding a radiopaque porous 4D-printed bioproduct for endovascular coiling. Extortionate researchers are trying to fabricate and design gland tissues through 4D bioprinting. The current oncological challenge is to develop in-vitro models for the tumor microenvironment. Kwag et al. [348] developed a PEGDA/GelMA-based bi-layered hydrogel by seeding SUM159 cells. These curved, tubular, and folded biocompatible constructs are considered vital for evaluating in-vitro models of ductal carcinoma. The application of 4D printing technology has emerged at the cellular scale. In research by Booth et al. [302] the tissue-like structure was printed with water in the oil droplet method. They printed cell-free expression into an oily environment, and after that, by employing external light stimuli, they were able to mimic a functional neuronal transmission.

4. Concluding remarks and future perspectives

Hi-tech 4D bioprinting, a cutting-edge technology, exhibits excellent control in automation and develops customized parts of intricate products by processing digital medical images. This technology is expanding and creating new avenues of research in biomedical fields by constructing and designing 3D cell-laden dynamics structures [351]. Recently, extortionate researchers are demonstrating the development of different stimuli-responsive polymers through 4D bioprinting and evaluating their biomechanical properties by considering different clinical practices including biosensors, actuators, TERM, wound healing, and DDSs [352–356]. This section also addresses RQ1, RQ2, and RQ3 and according to the literature, the following are the current challenges of 4D bioprinting which must be overcome for successful translation of these smart polymers in clinical applications.

The literature shows that the different intelligent materials especially smart polymers are highly sensitive to physical, biological, chemical, or combination of these stimuli (RQ2). These smart polymers along with 4D bioprinting technology are the future of the biomedical industry. The following are the research avenues that needed to be explored in the near future (RQ3): **(i)** Exploration of novel multi-stimuli materials; **(ii)** empirical modeling requirement; **(iii)** improvement in the biocompatibility and interlinking of the vascular tissues and **(iv)** commercialization of 4D bioprinting technology.

Exploration of novel multi-stimuli materials: The 4D-printed polymer products developed for biomedical industries should be able to transform their shape based on external stimuli as well as satisfy the demands of 3D bioprinting [357]. Presently, most of the available polymeric materials and hydrogels are sensitive to a single stimulus only, whereas, multi-stimuli sensitive 4D-bioprinted products undergo simple deformation such as curling, folding, and bending, which hinders the utilization of multi-responsive materials in the intricate microenvironment of the human body. Brisk efforts are needed to explore and develop novel multi-responsive SMPs and hydrogels. Additionally, the reinforcement of nanomaterials including ceramics, graphene, and MNPs into SMPs and hydrogels can help to construct multifunctional bioengineered tissues with extraordinary biomechanical properties.

Empirical modeling requirement: 4D bioprinting technology is opening new frontiers for developing printed products, and it possesses the propitious potential to revolutionize DDS and TERM. However, it possesses several limitations like structural robustness into design and prediction of 4D-printed structures. Therefore, focused research on the empirical modeling of this technology is needed to tackle these issues.

Accessibility of appropriate bioink materials and bioprinters: The accessibility of appropriate bio-ink materials is another issue that requires the attention of the biomedical community. 4D bioprinting has been applied in tissue grafting applications where there is a need to develop innovative bioink materials that would possess excellent multi-stimuli sensitivity, dynamic behavior, cellular adhesion, and adequate stiffness for in-vitro analysis. In addition to the above requirement of bioink materials, 4D bioprinting technology also requires novel bioprinters, mechanisms, and structural designs. Table 3 summarizes the specifications and cost of the commercially available bioprinters. Recently, some companies have developed bioprinters of low cost, therefore, the accessibility of these bioprinters will transform the landscape of the bioprinting market.

Improvement in the biocompatibility and interlinking of the vascular tissues: The vascular system of organs and tissues is dependent on the interlinking between tissue-specific cells and vascular cells [358]. This interlinking also depends upon the cell types and contents, thus requiring attention while designing co-cultured tissue regenerative systems. Recent advancements in the design of bioreactors including the addition of local tissues in the physiological environment have exhibited excellent prospects for developing intricate heterogeneous tissues. Despite advancements in 4D bioprinting technology, efforts are required to improve the biomechanical performance of vascular tissue grafts. There is still a need to replicate the biological functionality and structural complexity of in-vivo vascularization. Additionally, the integration of vascular tissues into living material is another challenge that requires the attention of scientists. Biomedical engineers should consider non-thrombogenic cardiovascular TE for controlling biological behavior in the future.

Commercialization of 4D bioprinting technology: The commercial utilization of 4D bioprinting technology in the biomedical sector is still limited (RQ1). The challenges hindering the commercialization of 4D bioprinting technology provide an opportunity to conduct strength, weakness, opportunity, and threat (SWOT) analysis, which has been illustrated in Fig. 27. Technology readiness level (TRL) is an assessment tool used to assess, analyze, and manage the risk caused by the particular technology [359]. TRLs for different biomedical applications are elaborated in Fig. 28.

By addressing all these challenges, 4D bioprinting of polymer-based biomaterials will enhance its utilization in different TERM applications including bone, cardiac, neural, cartilaginous, skin, DDSs, medical devices, and personalized medicine. Furthermore, the significant advancements in the current form of 4D printing technology will give an insightful understanding of stimuli-response materials, their features, and potential applications in the biomedical sector. In addition to the TERM applications, 4D bioprinting technology can also be used for organ replacement in serious injuries or chronic diseases in the near future.

Table 3
Overview of commercially available different bioprinters.

Commercial bioprinters	Country	AM technology	Build volume (mm^3)	Commonly employed materials	Price
Envision TEC's 3D bioplotter manufacturer series + Developer series	Germany	Syringe-based extrusion	150×150×80	Hydrogels, silicone, hydroxipatite, titanium, chitosan	>$200,000
RegenHU's 3D discovery + Biofactory	Switzerland	Syringe-based extrusion	60×60×55	Hydrogel, bioink, osteoink	>$200,000
BioBots	United States America	Syringe-based extrusion, blue light technology	90 × 90 × 90	Agarose, collagen, alginate, PEG	$10,000
BIONOVA X + Cellink company	Sweden/ United States America	DLP	9 × 9 × 9	Bioinks, hydrogels	–
Bioassembly bot series	United States America	Syringe-based extrusion	*305 × 254 × 178*	Hydrogels, PEG, gelatin, alginate, collagen	>$160,000
GeSim's Bioscaffolder 2.1	Germany	Syringe based extrusion and piezoelectric nanoliter pipetting	124 × 345 × 40	High viscosity pastes, alginate, calcium phosphate, silicon, cells and protein solutions	$180,000
3Dynamic Systems' alpha & Omega series	United Kingdom	Syringe based extrusion	150 × 150 × 60	Bone tissue from PCL, PLA, PGA, PEG, fibrin elastin, collagen, calcium phosphate and hydrogel mixtures	£12,000-18,000

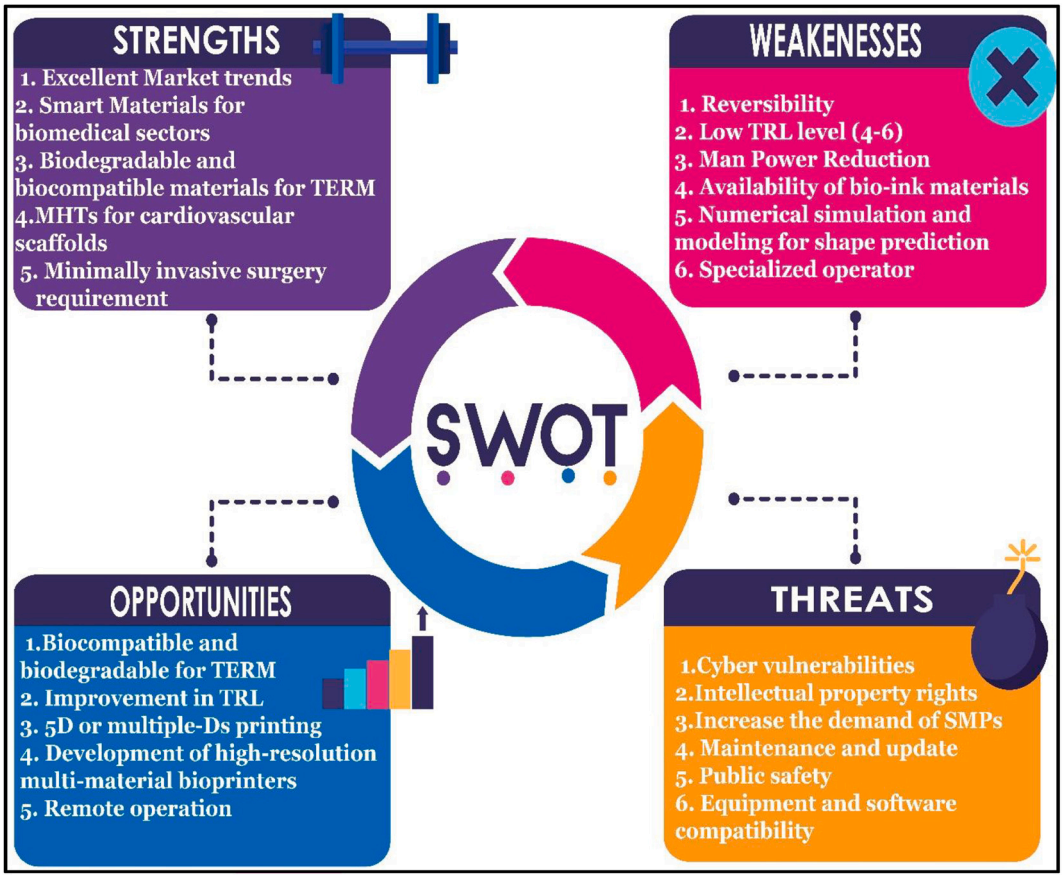


Fig. 27. SWOT analysis of 4D bioprinting technology.

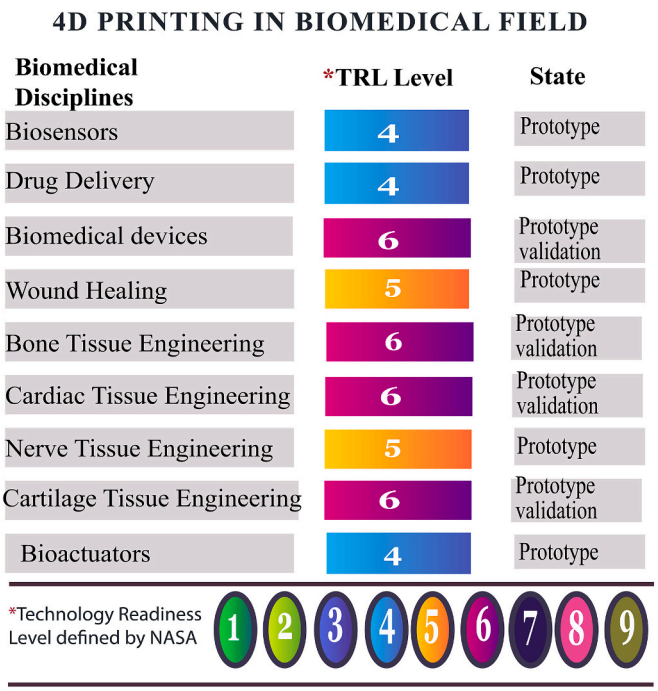


Fig. 28. TRLs of 4D-printed polymeric materials for biomedical applications including bone, cardiac, neural, cartilage, skin, drug delivery, biosensors, and actuators.

Funding

This work was not supported by any funding.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

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