Smart Hydrogel-Based Mechanical Metamaterials: A Review

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Abstract

Mechanical metamaterials have garnered significant attention due to their extraordinary mechanical properties derived from structural design and their potential for enabling new material applications. Although hydrogels present challenges in the fabrication of mechanical metamaterials due to their intrinsic high-water content, their inclusion is desirable because of their diverse responsive properties. This distinctive responsiveness, in combination with their extraordinary mechanical characteristics, opens up new possibilities for smart applications in fields such as biomedical engineering, soft robotics, and sensors. In the past five years, advancements in hydrogel fabrication techniques such as additive manufacturing and multi-material approaches have enabled the design of more complex and customizable hydrogel macro- to nanostructures, thereby advancing research on hydrogel-based mechanical metamaterials. This review offers recent insights into hydrogel materials as mechanical metamaterials, highlighting their development in diverse applications by harnessing hydrogel characteristics. It discusses various mechanical metamaterial characteristics, including negative hydration expansion, auxetic behavior, geometric transformation, and programmable mechanical properties, while also addressing current challenges and charting future prospects in the field.

1. Introduction to Smart Hydrogel-Based Mechanical Metamaterials

Mechanical metamaterials have recently emerged as a promising class of materials due to their great applicational versatility and uniquely high mechanical performance, such as a negative Poisson's ratio and extreme stiffness, which outshine conventional materials[1-5]. These exceptional mechanical properties stem from their structural design rather than their material constituents[6, 7].

A wide range of mechanical metamaterials has been reported, utilizing metallic[8], ceramic[9], polymeric[10], and foam materials[11] as their base. They are fabricated with engineering techniques ranging from the macro to nanoscale, which enable specific structural designs to be tailored and achieve a unique mechanical behavior[12-14]. However, hydrogel-based mechanical metamaterials present unique challenges compared to other base materials. Due to their primary composition of water, hydrogels exhibit inherent instability and sensitivity to environmental factors such as temperature, pH, and ionic strength, leading to significant alterations in their behavior under different conditions[15-19]. The swelling behavior of hydrogels also complicates the design and predictability of metamaterial behaviors[20, 21]. Most importantly, their lower mechanical strength and stiffness compared to metals, ceramics, or polymers introduce complexities in fabrication[22-25]. This softness poses challenges in manufacturing processes such as vat photopolymerization three-dimensional (3D) printing, often leading to diminished structural integrity and precision compared to more rigid base materials[26-28]. Furthermore, fabricating multi-material hydrogels is also challenging due to differences in their swelling and responsive properties and low adhesion with other materials[29, 30].

Despite these challenges stemming from inherent hydrogel characteristics, hydrogels remain highly promising candidates for mechanical metamaterials due to their diverse functional and responsive properties. These properties enable hydrogels to respond to external stimuli such as temperature[31, 32], pH[33, 34], light[35, 36], or electric fields[37] with greater sensitivity than other materials. The distinctive responsiveness of hydrogels, combined with the exceptional properties of mechanical metamaterials, opens up numerous new possibilities beyond those afforded by other materials, facilitating their evolution into smart mechanical metamaterials, where they can dynamically adapt their mechanical behavior or shape in response to changing environmental

conditions or user-defined triggers. Recent research has increasingly focused on developing hydrogel-based mechanical metamaterials, utilizing their unique characteristics through various fabrication approaches to address current challenges. These approaches involve integrating hydrogels with stiffer materials to create multi-material structures[38-42]. Advanced design techniques and computer simulations such as the finite element method (FEM) and artificial intelligence (AI), are also employed to optimize the structural and functional performance of these metamaterials[43-48]. Additionally, molecular-level architecture is used to tailor the properties of metamaterials at a local scale[49-51]. These efforts have resulted in the development of innovative smart hydrogel-based mechanical metamaterials in recent years, enhancing their functionality and applications through the incorporation of hydrogel responsiveness.

This review particularly focuses on hydrogel materials as mechanical metamaterials and aims to illustrate advancements in the recent development of smart mechanical metamaterials by harnessing properties inherent in hydrogels. In Section 2, the review categorizes hydrogel-based mechanical metamaterials into four main types based on their mechanical responses (Figure 1), while specialized ones such as radio-frequency-based mechanical metamaterials[52], acoustic impedance mechanical metamaterials[53], and bandgap-tunable mechanical metamaterials[54] are excluded. Section 2.1 discusses negative hydration expansion mechanical metamaterials which contract rather than expand when hydrated and offer precise control over volumetric changes. Auxetic mechanical metamaterials with a unique negative Poisson's ratio and exhibit unconventional deformation behaviors are discussed in Section 2.2. Section 2.3 covers geometric transformation mechanical metamaterials, which undergo specific shape changes in response to mechanical stress. In Section 2.4, programmable mechanical metamaterials are explored for their broad range of stiffness or toughness in adaptive material applications. Finally, Section 3 addresses

current challenges and future prospects in this field to inspire further research and innovation in smart mechanical metamaterials, drawing from ongoing advancements in functional hydrogel research.

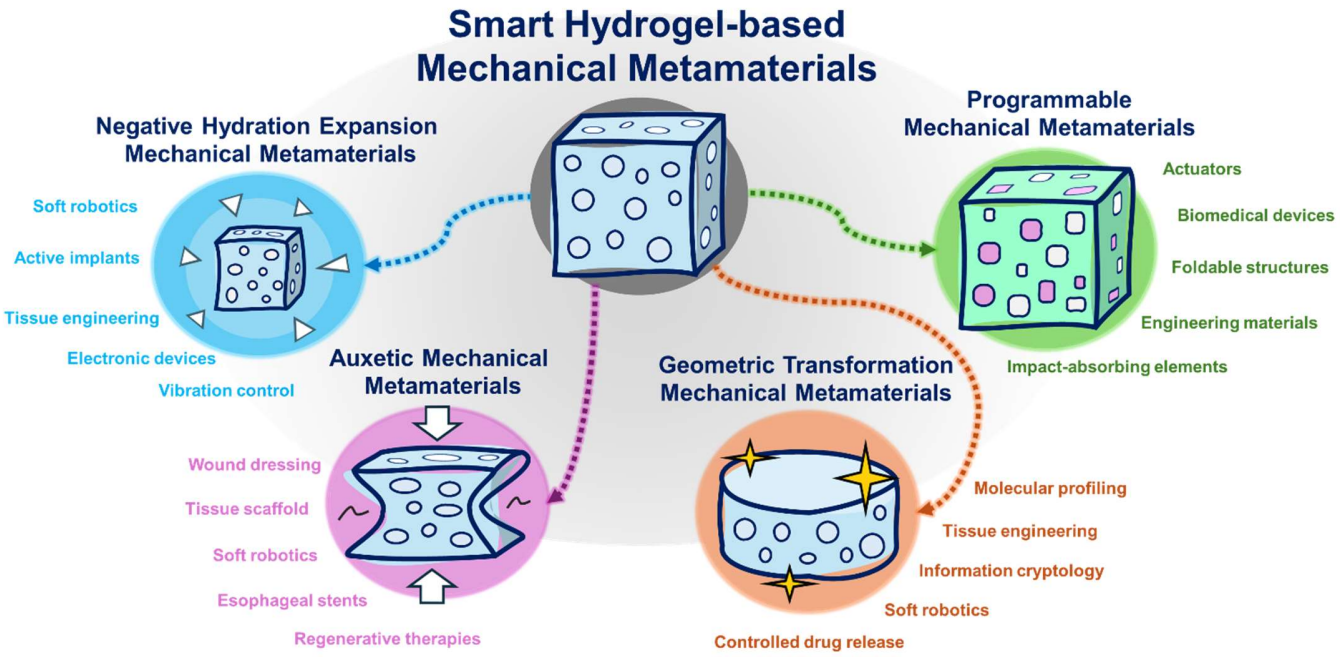

Figure 1. Overview of research on hydrogel-based mechanical metamaterials, including their classification and major applications.

2. Hydrogel-Based Mechanical Metamaterials

2.1 Negative Hydration Expansion Mechanical Metamaterial

Negative hydration expansion mechanical metamaterials exhibit a counterintuitive behavior upon hydration: they contract when hydrated and expand when dehydrated[55, 56]. This behavior is

opposite to typical hydrogels, which generally expand when absorbing water and contract when losing water[57]. The unique properties of negative hydration expansion mechanical metamaterials are achieved through precise structural design and material composition, allowing them to respond unusually to hydration changes. These metamaterials often involve intricate geometries and multi-material compositions with varying swelling capacities to produce the desired expansion and contraction behaviors[38-40]. This characteristic is unique to hydrogel-based mechanical metamaterials, as hydrogels exhibit significant swelling behavior not found in metals, ceramics, or polymers. Multi-material 3D printing is often utilized for their fabrications[38-40]. The water-responsive nature of hydrogels allows them to contract when hydrated and expand when dehydrated, making them especially suitable for applications requiring precise control over volume changes in response to moisture, such as sensors and adaptive structures, as outlined in Table 1.

Table 1. Summary of Negative Hydration Expansion Mechanical Metamaterial

No.	Material	Stimuli	Study method	Fabrication method	Example application	Reference
1	Hydrogel (Sup705), rubber elastomer (Tango Black Plus), polymer (RGD8530)	Solution	Experiments and FEM simulations	Multi-material 3D printer	Bioelectronics and Biological tissue engineering	38
2	Hydrogel (Sup705), rubber elastomer (Tango Black Plus), polymer (RGD8530)	Solution	Experiments, FEM simulations, and mathematical modelling	Multi-material 3D printer	Stretchable electronics, robotics, and bionic engineering	39
3	Hydrogel (Sup705), rubber elastomer (Tango Black Plus), polymer (RGD8530)	Solution	Experiments, Mathematical modelling, FEM simulations	Multi-material 3D printer	Soft robotics and active implants	40
4	Hydrogel (Sup705), rubber elastomer (Tango Black Plus), polymer (RGD8530)	Solution	Theoretical models and FEM simulations	-	Vibration control, active noise cancellation	41
5	Hydrogel and polymer	Solution	Theoretical analysis and FEM simulation	-	Electronic and biomedical devices	42

A highly adaptive negative hydration expansion mechanical metamaterial has been developed by Chen and colleagues using a hydrogel-based material composite combined with rubber elastomer and polymers[38]. They designed a mechanical metamaterial composite capable of an adjustable swelling behavior—positive (expansion), negative (contraction), or zero (stable) — by altering the orientation of circular holes and modifying the lattice structure geometry. They created a composite plate using 2D parallelogram cells with multiple layers: two encapsulation layers made of rubber elastomer (Tango Black Plus), two active hydrogel layers (Sup705), and a support polymer layer (RGD8530), employing a combination of experimental fabrication and FEM simulations (Figure 2a). This integrated approach allows for both experimental testing and

predictive modeling of the material's mechanical responses in hydrogel-driven origami metamaterial applications. The layers were printed using a multi-material PolyJet 3D printing machine (Objet350 Connex2, Stratasys), enabling the creation of complex structures with precise control over material properties. Specifically, the hydrogel can swell in positive, negative, or zero directions due to the orientation and design of small circular holes connecting the polymer and hydrogel layers, which regulate water flow and therefore influence the hydrogel's expansion by controlling the amount of water absorbed and the resulting swelling behavior (Figure 2b). The support and encapsulation layers restrict swelling, while the arrangement of the holes controls whether the hydrogel expands outward, contracts, or remains stable, enabling precise control of its behavior. In hydrogel-driven origami metamaterials, downward-facing holes facilitate water absorption and induce positive swelling, expanding the material. Conversely, upward-facing holes restrict water access, leading to negative swelling or contraction of the metamaterial. This capability is particularly valuable in bioelectronics and biological tissue engineering, addressing the need for adaptive materials that interact effectively with biological systems, offering tailored responses for applications like smart implants and tissue scaffolding.

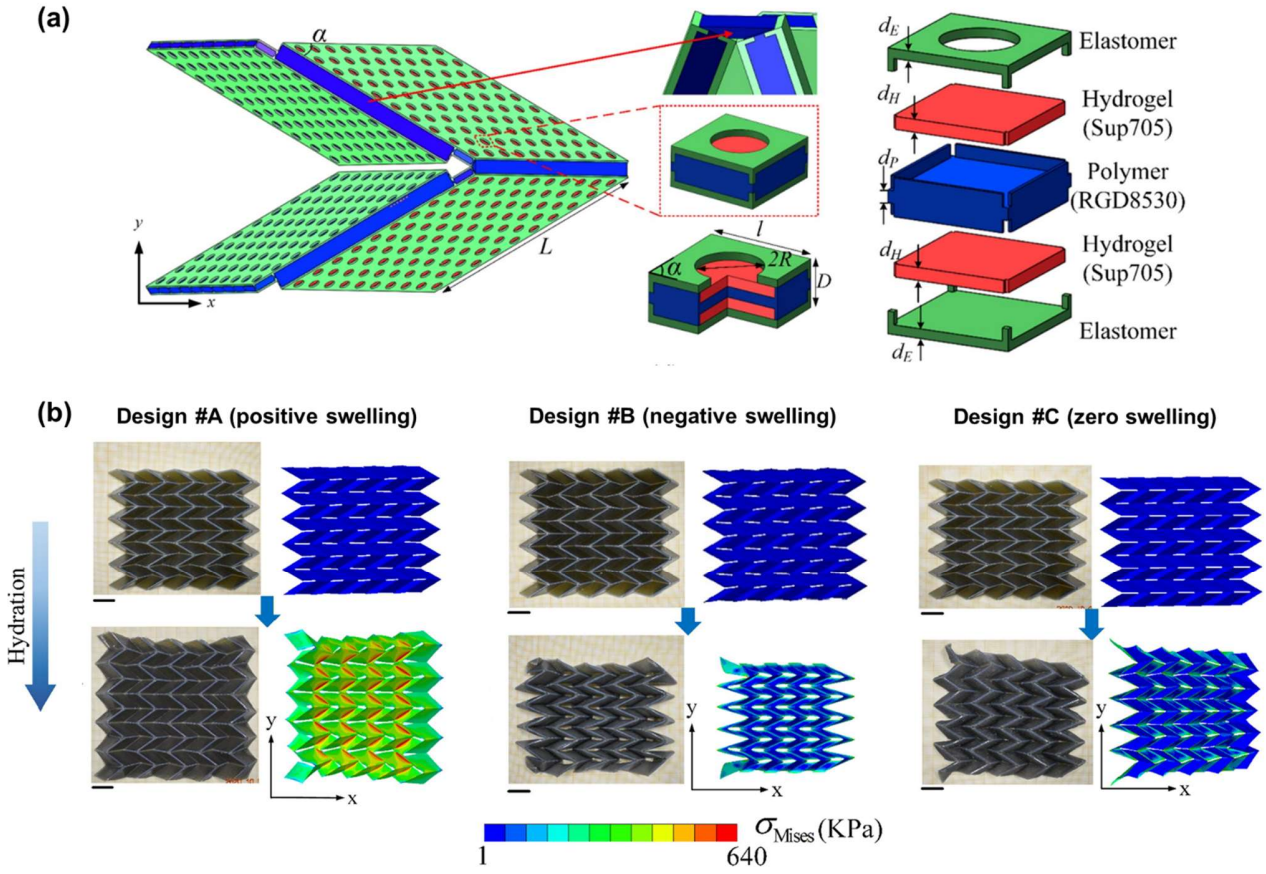

Figure 2. Hydrogel-driven origami metamaterials with tunable swelling behavior. (a) Schematic illustration of the hydrogel-based composite design, consisting of elastomer, hydrogel, and polymer layers. (b) Digital images and FEM results showing the hydration behavior of the origami metamaterials with different designs, demonstrating positive, negative, and zero swelling. Modified and reproduced with permission from [38].

Another work by Wei and colleagues utilized a similar composite metamaterial incorporating hydrogel, polymer (RGD8530), and rubber elastomer (Tango Black Plus), but they employed a different design strategy[39]. Using a multi-material 3D printer (Objet350 Connex2,

Stratasys), they fabricated 2D and 3D composite metamaterials with adjustable swelling behavior, which they describe as having isotropic negative hydration expansion properties, expanding uniformly in all directions when exposed to water. Their metamaterial features a re-entrant auxetic honeycomb structure, incorporating a composite lattice microstructure with a hydrogel driving layer and a re-entrant framework. This material exhibits negative hydration expansion because the hydrogel swells when exposed to water. This swelling creates a force that bends the material, particularly in structures like composite beam where the hydrogel's expansion is constrained by surrounding layers. This design effectively uses the swelling of the hydrogel to produce controlled bending motions, demonstrating its capability for negative hydration expansion. Effective negative hydration expansion coefficient depends on the length of the driving layer and the straight bar connecting the lattice structures. The negative hydration expansion coefficient of the lattice microstructure can be adjusted between 0% and -22.4% via modifying the geometric parameters. This adaptability enables tailoring the mechanical metamaterial's reaction to moisture and environmental factors, potentially enhancing its mechanical properties which is suitable for specialized uses in fields such as stretchable electronics, soft robotics, and bionic engineering. Additionally, this work integrates evidence from experiments, FEM simulations, and theoretical models to enhance understanding of how hydrogel-driven metamaterials respond to expansion under varying conditions.

Ma and colleagues also developed a water-driven mechanical metamaterial capable of negative swelling[40]. They utilized multi-material 3D printing (Objet350 Connex2, Stratasys) to fabricate composite samples consisting of hydrogel, polymer (RGD8530), and rubber elastomer (TangoBlackPlus, Stratasys), similar to the two previously mentioned works. However, instead of focusing on constrained geometries, they emphasize chiral deformation principles, where the

arrangement of chiral structures dictates specific bending and deformation patterns as the hydrogel swells and contracts (Figure 3a). This is demonstrated through FEM simulation and theoretical models. The metamaterial exhibits bi-directional reversible negative expansion deformation. This enables it to undergo controlled deformation cycles in response to stimuli like water absorption and drying, returning to its initial shape afterward (Figure 3b and c for experimental and FEM results, respectively). The shrinkage and recovery process during hydration and dehydration of the metamaterials shows effective negative expansion hygroscopic ratios ranging between −57.1% and −62.3%, which are controllable by adjusting lattice geometry and microstructural parameters. Such reversible behavior is advantageous for applications requiring extreme configuration change and precise motion control, such as soft robotics and adaptive structures in biomedical devices like active implants.

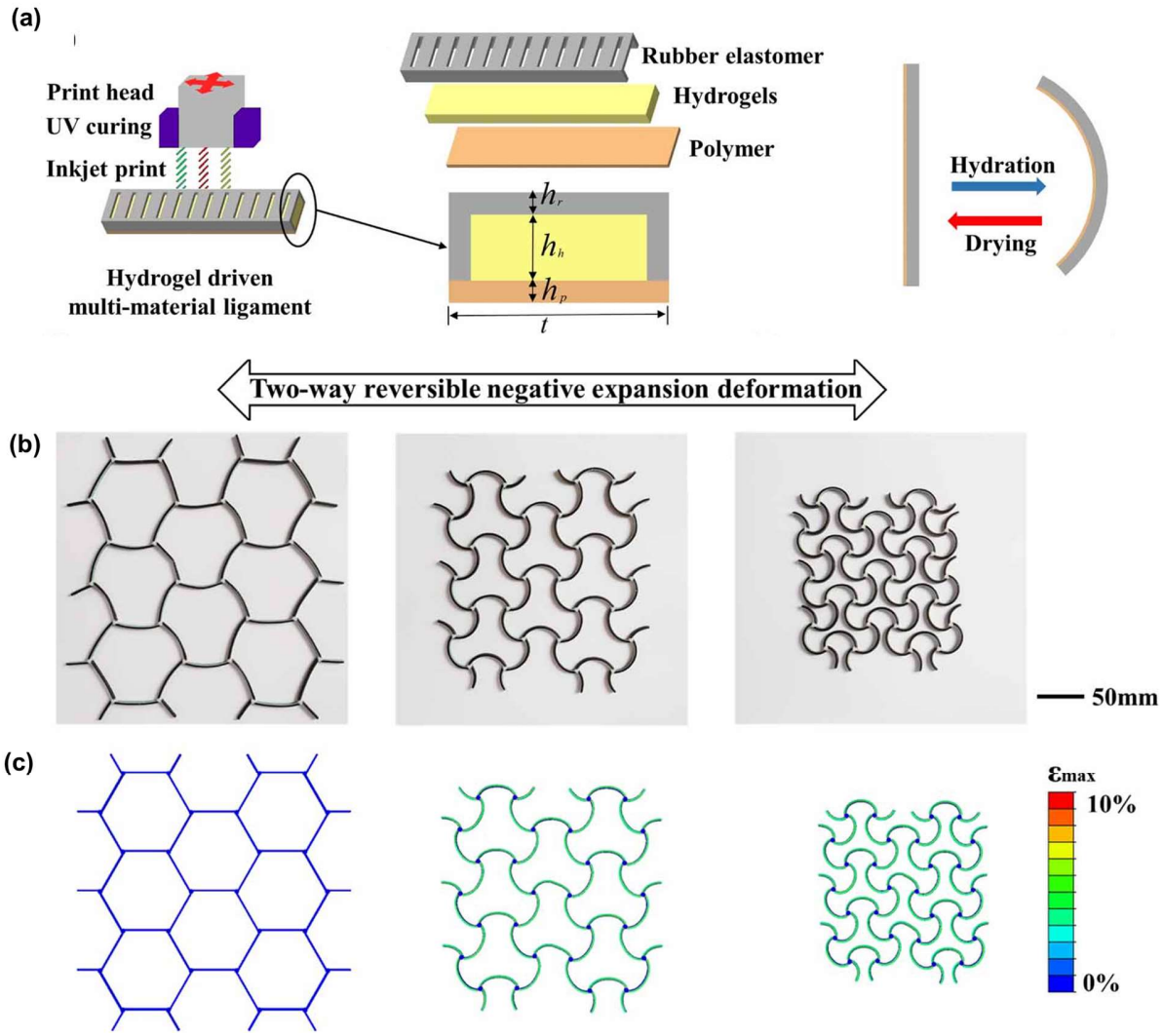

Figure 3. Hydrogel-based chiral metamaterial exhibiting negative swelling. (a) Preparation and design strategy of the negative swelling chiral metamaterial, consisting of elastomer, hydrogel, and polymer layers. (b) Experimental results showing the negative expansion deformation behavior of the hydrogel-based chiral metamaterial. (c) Finite element simulation results showing the negative expansion deformation behavior of the hydrogel-based chiral metamaterial. Modified and reproduced with permission from [40].

Tao and colleagues designed and fabricated a flat two-dimensional, planar surface metamaterials that utilize hydrogel swelling to achieve various bending deformation modes through theoretical modeling and numerical simulation[41]. These include positive and negative swelling, as well as various deformation modes: isotropic, anisotropic, gradient, and bending deformations. The metamaterial's unit cell is formed by connecting end-to-end composite beams at specific angles, comprising a rubber encapsulation layer (Tango Black Plus), an active hydrogel layer (Sup705), and a support polymer layer (RGD8530). These diverse deformation modes result from a structural design strategy that capitalizes on the deformation mismatch between the high-swelling hydrogel and the non-swelling elastomer within the bi-material composite beam. Inspired by star-shaped kirigami structures, the arrangement and geometric parameters of the composite beams enable precise control and modulation of these deformation modes. Fine-tuning the metamaterial's deformation behavior involves adjusting the thickness and length ratios of the active and support layers, as well as the angles between the composite beams. This study demonstrates the precise tunability of the metamaterial's band gap and elucidates its deformation characteristics through rigorous theoretical frameworks. Moreover, it provides a comprehensive understanding of metamaterial deformation behaviors and offer valuable insights for developing reconfigurable structures and customizable band gaps.

Another potential design strategy for hydrogel-based metamaterials with exceptionally large negative hygroscopic expansion was proposed by Ma and colleagues[42]. The design process integrates hydrogel and polymer materials into a specific lattice structure, where ligaments composed of hydrogel and polymer layers play a crucial role. This lattice structure features a regular arrangement of interconnected elements forming a repeating pattern throughout the material (Figure 4). By harnessing the unique properties of hydrogels, such as their high-water

absorption capacity and swelling behaviour, the researchers engineered these ligaments to induce controlled mechanical deformations in response to external stimuli, effectively controlling the material's deformation behavior. Theoretical analysis and finite element simulations demonstrate that negative hygroscopic expansion behaviors originate from the designed deformation mechanisms. The designed 2D structure achieves effective linear strains of up to -57%, corresponding to area strains of up to -81%. Moreover, the 3D lattice microstructure exhibits an effective hygroscopic expansion ratio of approximately -92%, showcasing the significant negative hygroscopic expansion capabilities of the metamaterials. These findings, although based on theoretical analysis and FEM simulations, highlight the potential to achieve hydrogel-based mechanical metamaterials with significantly higher negative hygroscopic expansion ratios compared to previous studies[39, 40]. The design strategy offers insights into enhancing the negative hygroscopic expansion ratio of hydrogel-based metamaterials, with applications spanning electronic and biomedical engineering across different scales. All the aforementioned works on the negative swelling behavior of mechanical metamaterials require multi-material fabrication, involving not only hydrogels but also other materials to induce structural changes upon hydration or dehydration. Hence, the fabrication techniques play a crucial role in achieving the desired designs. Additionally, these works were supported by simulations such as FEM and theoretical models, which are essential for designing multi-material structures. This integration of strategic design and fabrication techniques is key to developing hydrogel-based negative hydration expansion mechanical metamaterials.

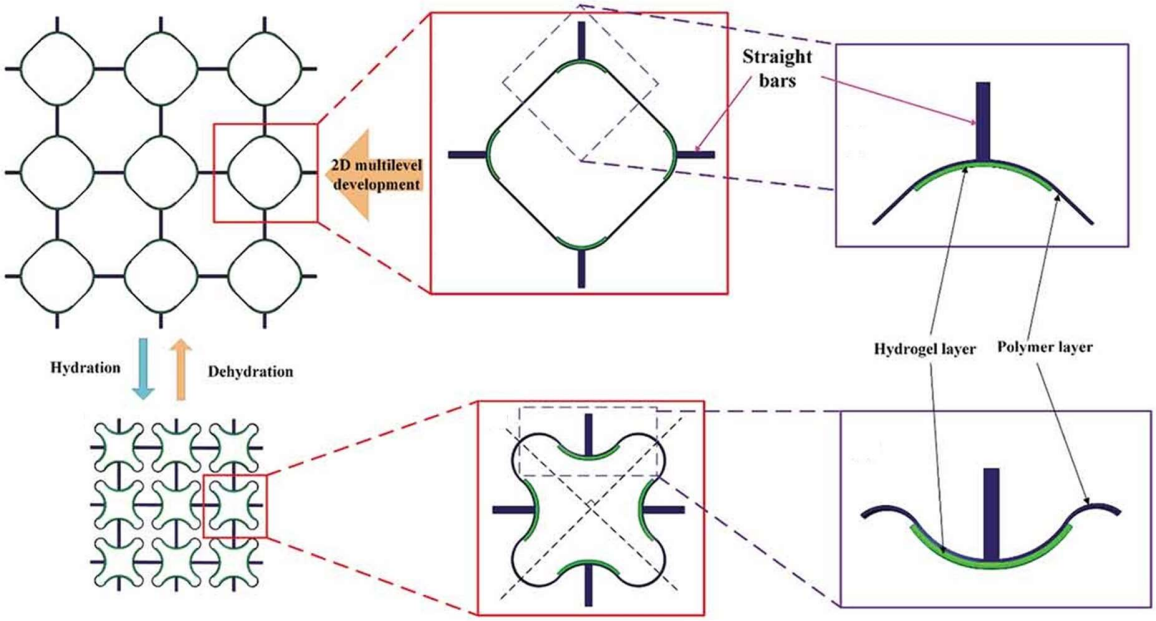

Figure 4. Hydrogel-based metamaterial with ultra large negative hygroscopic expansion ratio. Modified and reproduced with permission from [42].

2.2 Auxetic Mechanical Metamaterial

Auxetic mechanical metamaterials, with their unique negative Poisson's ratio, exhibit unconventional deformation behaviors[58-60]. These materials expand laterally when stretched and contract when compressed, contrary to the behavior of conventional elastic materials. Their special properties result from the engineering of their internal structure, which deforms in response to mechanical stimuli like tension or compression. The fabrication of auxetic hydrogels involves creating specific geometric structures within the material[61, 62]. Techniques such as laser cutting[63], 3D printing[64], molding, or templating[65] are employed to achieve these structures in the case of hydrogels, as shown in Table 2. By adjusting the geometry and composition of the materials, the degree of auxetic behavior can be finely controlled, making these hydrogels highly customizable

for various applications. Particularly, as hydrogels exhibit biocompatibility, several advanced biomedical applications have been identified when imparting auxetic characteristics into them.

One potential biomedical application of auxetic hydrogels has been demonstrated with an enhanced toughness hydrogel fabricated through digital light processing (DLP) 3D printing[64]. By combining 2-hydroxyethyl methacrylate (HEMA) with methacrylated cellulose nanocrystals (CNCMA) as a macro-cross-linking agent, Pruksawan and colleagues fabricated a hydrogel with a tensile strength of up to 143 kPa and a tensile modulus of up to 134.8 kPa, attributed to chemical and physical crosslinks between pHEMA and CNCMA (Figure 5a). This tough hydrogel was used in the fabrication of soft auxetic structures, including re-entrant hexagonal honeycomb and hexagonal honeycomb designs. The re-entrant hexagonal honeycomb structure exhibited auxetic behavior with a negative Poisson's ratio of -0.7, while the hexagonal honeycomb structure exhibited a regular positive Poisson's ratio of >0.5 (Figure 5b). Additionally, the re-entrant hexagonal honeycomb auxetic structure provided greater toughness and stretchability compared to non-auxetic hexagonal honeycomb structures, enhancing mechanical performance and applications in mechanical metamaterials. One demonstrated application is using these soft auxetic hydrogel structures as auxetic esophageal stents with a self-expandable design. Their negative Poisson's ratios and high fracture strain allow them to widen when pulled apart, forming a hollow tube to treat narrowed esophagus conditions.

Table 2. Summary of Auxetic Mechanical Metamaterial

No.	Material	Stimuli	Study method	Fabrication method	Example application	Reference
1	2-hydroxyethyl methacrylate (HEMA), methacrylated cellulose nanocrystals (CNCMA)	External force	Experiment	DLP 3D printing	Auxetic esophageal stents	64
2	HEMA, polyethylene glycol dimethacrylate (PEGDMA), acrylic acid	External force and pH	Experiment	DLP 3D printing	Auxetic hydrogel wound dressing	66
3	Polyethylene glycol diacrylate (PEGDA), and gelatin methacryloyl (GelMA)	External force	Experiment	UV photopolymerization	Biomimetic organ patch	67
4	PEGDA, and acrylic acid	External force	Experiment and FEM simulation	Digital micromirror device projection printing	Regenerative tissue scaffold	45
5	PEGDA, and acrylate-PEG RGDS peptide	External force	Theoretical modelling and Experiment	Femtosecond laser technology	Mechanobiology	68
6	Acrylamide, stearyl methylacrylate, acrylic acid, thermoplastic polyurethane (TPU), polyacrylamide, benzophenone	External force and temperature	Experiment and FEM simulation	In-situ photopolymerization	Smart materials and scaffold design	43
7	Triethylene glycol methyl ether acrylate (mTEGA), diethylene glycol ethyl ether acrylate (eDEGA), acrylamide, alginate	External force and temperature	Experiment and FEM simulation	Sequential photopolymerization	Soft robotics	44
8	Poly(Vinyl alcohol) (PVA), polyethylene glycol octyl phenyl ether	External force	Experiment	Freeze-thaw	Pressure-release implants	49
9	2-acrylamido-2-methyl-1-propanesulfonic acid, and polytetrafluoroethylene (PTFE)	External force	Experiment	Suspension polymerization	Regenerative therapies for intervertebral disc degeneration	69

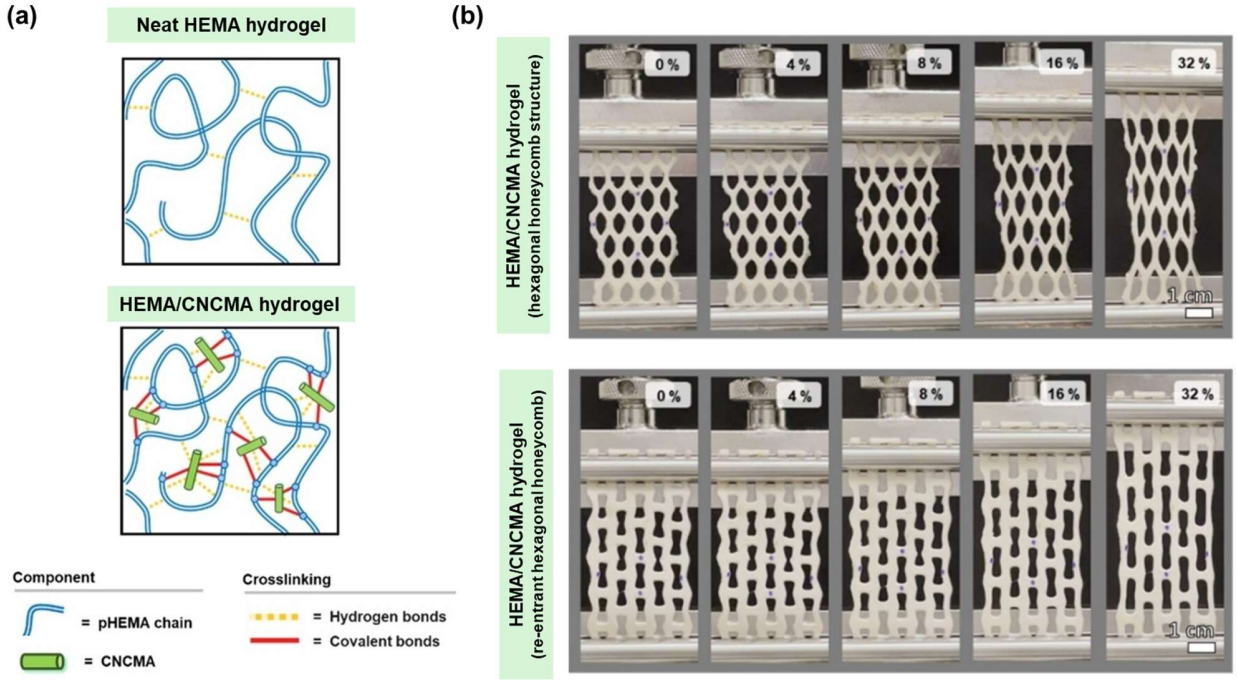

Figure 5. 3D-printed tough hydrogels incorporating methacrylated cellulose nanocrystals (CNCMA) and their auxetic structures. (a) Schematic illustrating the crosslinking network comparison between neat HEMA hydrogel and HEMA/CNCMA hydrogel. (b) Demonstration of the mechanical auxetic behavior in printed hydrogels featuring different structures: hexagonal honeycomb and re-entrant hexagonal honeycomb. Modified and reproduced with permission from [64].

Another application of auxetic hydrogels is as wound dressing hydrogels. Tsegay and colleagues demonstrated that auxetic hydrogels could serve as 3D printable pH indicator wound dressings[66]. The hydrogel is composed of HEMA monomer, polyethylene glycol dimethacrylate (PEGDMA) crosslinker, with 5% acrylic acid added for greater flexibility. This hydrogel exhibits

a tensile strength of 3.5 MPa, a Young's Modulus of 78.9 MPa, and a failure strain of 4.5%. The balance between strength and flexibility, along with its biocompatibility, makes it suitable for use as a wound dressing that can effectively isolate the wound and promote enhanced healing. They 3D printed an auxetic wound dressing with a re-entrant structure, which features a negative Poisson's ratio, in a similar way to the previously discussed paper. This structure allows the dressing to expand laterally when stretched, increasing the covered wounded area and therefore effectiveness in wound care applications. To enhance the functionality of this auxetic hydrogel wound dressing, they integrated color change pH responsiveness into the hydrogel, enabling real-time monitoring of the wound's pH environment. This capability is crucial for assessing and promoting effective wound healing. Additionally, they developed a poly(acrylic acid) and water-based adhesive to securely attach the auxetic wound dressing to moving body joints, such as wrists or elbows. Thanks to the auxetic structure of the wound dressing, which exhibits a negative Poisson's ratio, it can closely follow and adapt to the movements of body joints without forming wrinkles or causing discomfort.

In addition to the fabrication of stents and wound dressing hydrogels, Chansoria and colleagues developed a hydrogel patch designed to mimic the dynamic behavior of organs, using digital light projection to create a bilayer structure[67]. The top layer, made of polyethylene glycol diacrylate (PEGDA), prevents fouling and ensures biocompatibility, while the bottom layer, gelatin methacryloyl (GelMA), supports cell adhesion and mimics natural tissue behaviors like anisotropy and auxetic properties. They fabricated the patch by crosslinking GelMA at room temperature and adding the PEGDA layer under UV light with a photoinitiator. Their approach involved screening over 116 patch designs and using in silico modeling to select designs with auxetic behavior and tailored mechanical properties. This systematic process allowed them to

create versatile patch architectures that replicate the mechanics of organs such as the lung, heart, stomach, bladder, intestines, and skin. This mechanically responsive hydrogel patch holds promise for medical applications, including biomimetic organ patch development and treating conditions like chronic wounds, pneumothorax, and cardiac diseases, demonstrating its versatility in clinical use, similar to the two papers above.

In addition to their various clinical applications, the use of auxetic hydrogels as scaffolds in biomedical engineering has also been investigated by Fozdar and colleagues[45]. They explore acrylated-PEG hydrogel, known for creating porous scaffolds that support bone marrow cell growth. They utilize digital micromirror device projection printing (DMD-PP) for precise scaffold design, with their hydrogel precursor including PEGDA, and acrylic acid. Their approach involves refining the auxetic properties of 3D polymer scaffolds by precisely adjusting the geometrical configurations of their unit cells, including variations such as re-entrant honeycomb, cut missing-rib, and intact-rib architectures (Figure 6a). This allows for tailored mechanical responses and enhanced elasticity under specific loading conditions. Their single-layer scaffolds exhibited the expected auxetic behavior, achieving Poisson's ratios such as approximately -2.7 to -0.8 for re-entrant structures (Figure 6b). This behavior remained consistent when scaling up production to multiple layers. They successfully fabricated a triple-layer scaffold, demonstrating their method's capability to handle complex designs. By combining theory with experiments, they confirmed and predicted the mechanical behavior of these scaffolds, crucial for developing customized solutions in regenerative medicine by extension.

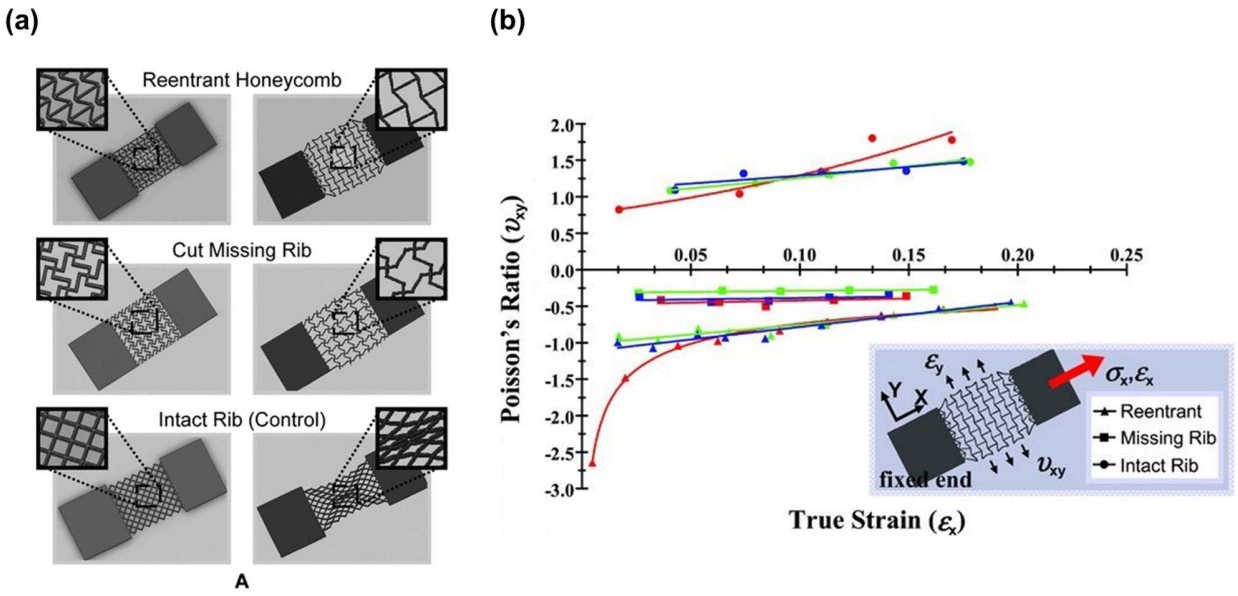

Figure 6. 3D-printed polyethylene glycol (PEG) scaffolds with tunable negative Poisson's ratios. (a) Illustration of single-layer polyethylene glycol (PEG) constructs composed of unit cells with re-entrant honeycomb, cut missing-rib, and intact-rib architectures. (b) Experimental measurements of Poisson's ratio as a function of true strain for the single-layer PEG constructs of unit cells with re-entrant honeycomb, cut missing-rib, and intact-rib architectures. Different colored marks and lines indicate separate experimental measurements. Modified and reproduced with permission from [45].

Apart from creating physical constructs that display auxetic behavior, auxetic hydrogel structures have also been utilized biologically by incorporating cells to enhance their mechanical properties. Zhang and colleagues engineered these hydrogels to explore the effects of varying mechanical stiffness on cellular responses[68]. They utilized PEGDA due to its biocompatibility and adjustability in stiffness. Employing femtosecond laser technology, they fabricated PEGDA

structures with tunable Poisson's ratios, including suspended web designs that exhibited both positive and negative Poisson's ratios. Cell experiments involving 10T1/2 fibroblast cells revealed that structures with negative Poisson's ratios experienced significantly greater deformation under cellular forces compared to those with positive Poisson's ratios. This deformation influenced cellular behaviors such as adhesion, migration, and notably, cell division, where negative Poisson's ratios structures led to abnormal retention of midbody structures during cytokinesis. The precise control of Poisson's ratio in biomaterials thus showing considerable potential for advancing mechanobiology studies.

Another worthy contribution in the realm of auxetic hydrogel metamaterials lies in their potential for programmability, which introduces further unique and diverse applications in adaptive mechanical metamaterials elaborated below. Du and colleagues introduced a mechanically programmable composite metamaterial capable of switching between positive and negative Poisson's ratios[43]. These materials combine a robust thermoplastic polyurethane (TPU) frame with soft, hydrogel-based fillers to customize their mechanical properties (Figure 7a). Initially, a flexible lattice structure is 3D-printed using TPU, followed by injection of a liquid hydrogel prepolymer (polyacrylamide) into the lattice voids and polymerization with UV light. Strengthening the bond between TPU and hydrogel, benzophenone is used to modify the lattice structure's surface before polymerization, significantly enhancing bond strength and toughness. The study demonstrates precise control over auxetic properties by systematically varying the Young's modulus ratio (E_m/E_f) of the frame and filler, resulting in Poisson's ratios ranging from approximately -0.5 to 0.27 and significant variations in effective Young's modulus (E_{eff}) (Figure 7b and c). This tunable mechanical behavior allows the material to dynamically switch between negative and positive Poisson's ratios, highlighting its adaptability for applications such as

controlling sound frequencies through structural adjustments. This programmable approach could open up new possibilities in electronics and smart materials.

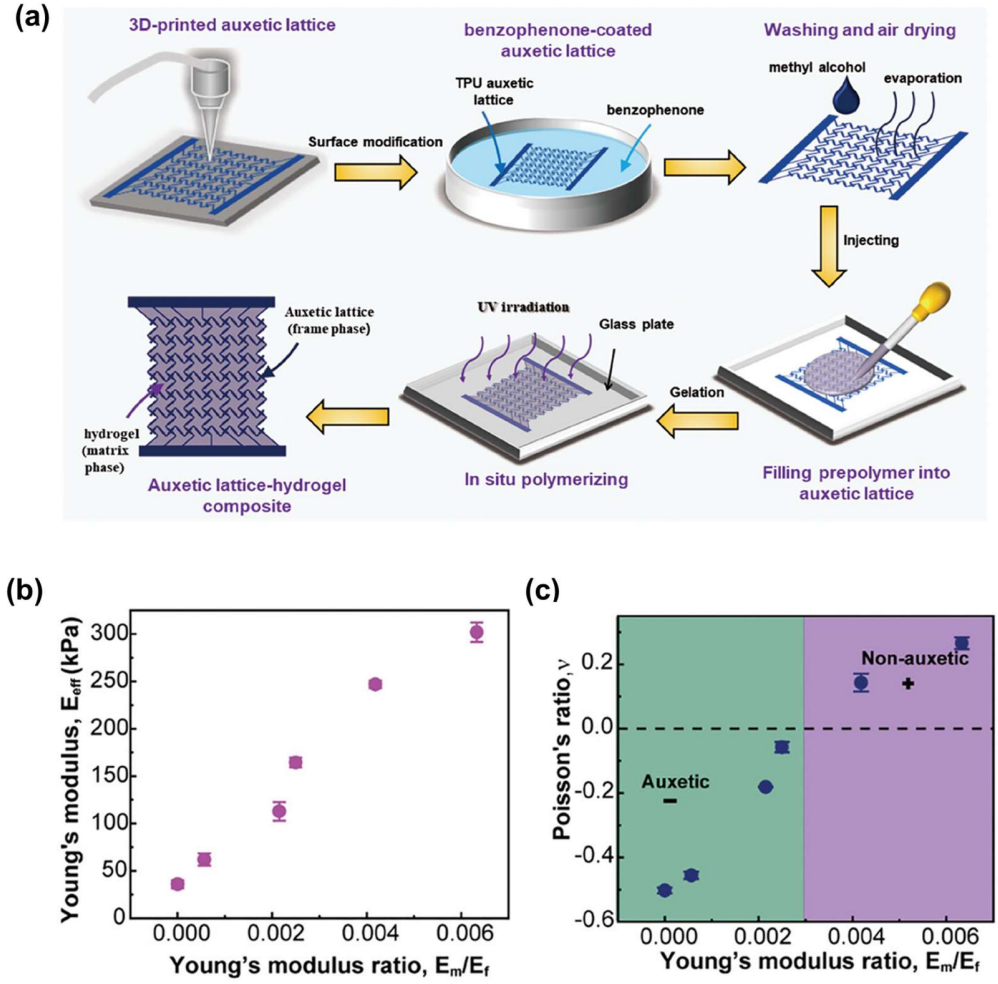

Figure 7. Mechanically programmable composite metamaterials with switchable positive and negative Poisson's ratio. (a) Schematic illustrating the fabrication process of the auxetic lattice-hydrogel composite, featuring an auxetic lattice as the frame phase and hydrogel as the matrix phase. (b) and (c) Effective Young's modulus (E_{eff}) and Poisson's ratio of the obtained composites plotted as a function of the Young's modulus ratio of the frame and filler (E_m/E_f). Modified and reproduced with permission from [43].

Building on efforts to achieve programmable auxetic properties, Skarsetz and colleagues have also explored their potential through the use of shape-changing hydrogels[44]. They developed a shape-changing hydrogel metamaterial by strategically placing responsive elements to achieve programmable auxetic properties, along with analysis by FEM simulation. The metamaterial consists of two layers: a non-responsive acrylamide crosslinked with N-N′-methylene bisacrylamide (passive layer) and an alginate crosslinked with $CaCl_2$ (active layer). This double network structure enhances mechanical strength and crack resistance. Sequential photopolymerization and molds with a re-entrant structure were used to create this design, allowing it to deform repeatedly without breaking. The metamaterial responds to environmental and mechanical stimuli. Environmental responsiveness occurs with temperature changes, transforming its structure from re-entrant to honeycomb. Mechanical responsiveness involves changing its Poisson's ratio under tensile strain. Such auxetic behaviour were verified with the use of FEM simulations. Potential applications include adaptive mechanical metamaterials with reversible behaviors, and uses in mechanical computing, soft robotics, robotics, tissue engineering, and soft implants due to its flexibility and programmability. This work introduces a novel concept where the metamaterial's structure can be reconfigured post-manufacturing through a shape-morphing approach. The concept can extend to more layers, different architectures, hydrogel formulations, and environmental conditions, offering new design possibilities in shape-changing hydrogel metamaterials.

Several hydrogel-based auxetic mechanical metamaterials have been developed primarily for biomedical applications, leveraging the unique properties of hydrogels, as discussed earlier. However, most of these metamaterials achieve their auxetic characteristics through macro-

structure design using fabrication techniques such as DLP 3D printing, DMD-PP, or mold casting to meet the desired structural requirements. In these methods, the auxetic characteristic originates from the structural design rather than the intrinsic properties of the hydrogels. Therefore, the material used does not directly determine the mechanical metamaterial characteristics. Despite this, the auxetic properties of hydrogels can be expanded beyond the limitations of macro-scale design. Ma and colleagues demonstrated this by fabricating auxetic hydrogels through micro-scale engineering methods[49]. They fabricated poly(vinyl alcohol) (PVA) hydrogels with closed-cells, internally concave pores (IICP) and interconnected pores (ICP), showcasing diverse micro-cell structures (Figure 8a, b and c). The variation in pore size, shape, and distribution led to local Poisson's ratios ranging from -0.8 (auxetic, negative) to 0.1 (conventional, positive) at the microscale (Figure 8d). The preparation of PVA hydrogels with closed cells involved dissolving type 17–99 PVA powders in deionized water to form a 15 wt.% hydrosol, mixed with polyethylene glycol octyl phenyl ether (OP, TX-10) as a pore-forming agent, followed by freeze-thaw cycles and washing. For PVA hydrogels with IICPs, compression after initial freeze-thaw cycles induced concave pore formation, while ICPs were created by incorporating NaCl particles and OP, which were later removed via leaching. Using the digital speckle correlation method (DSCM), the researchers analyzed these hydrogels' microstructures and calculated their varying local Poisson's ratios, indicative of their elastic responses to mechanical compression. With their robust mechanical properties, non-toxicity, and biocompatibility, these PVA hydrogels hold promise for biomedical applications such as implants, drug delivery coatings, porous materials, and composite structures.

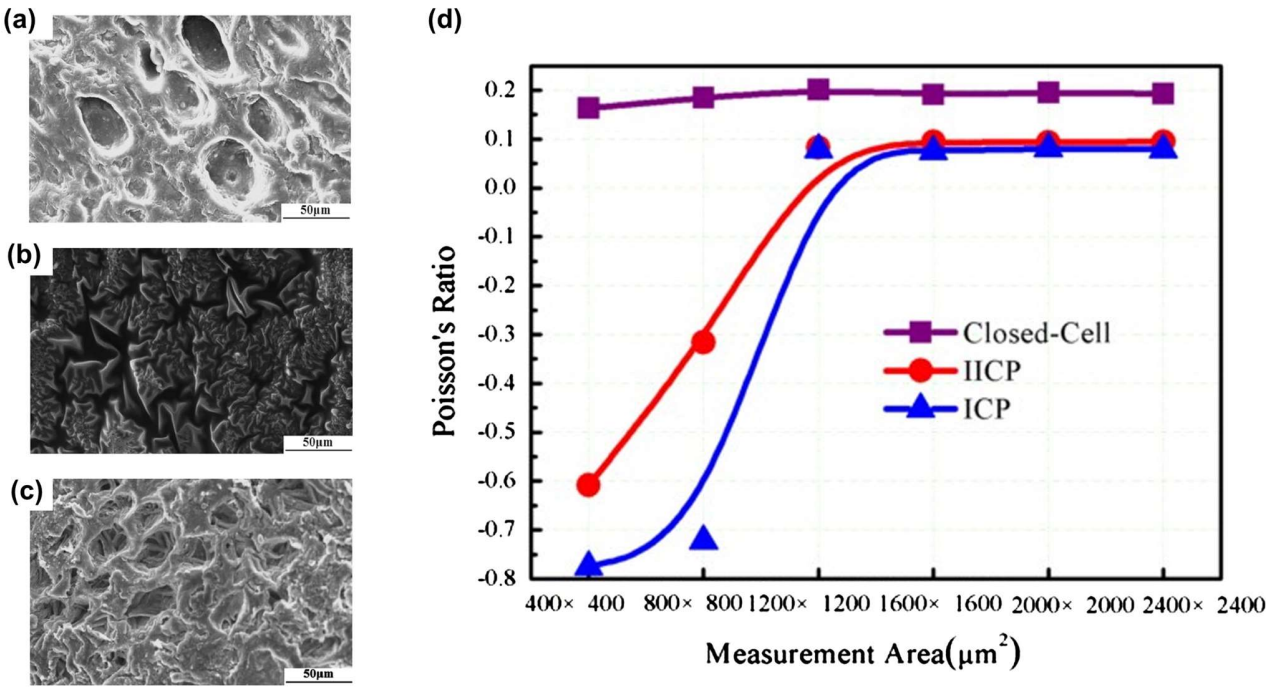

Figure 8. Morphology and corresponding local Poisson's ratio of poly(vinyl alcohol) (PVA) hydrogels. (a) Morphology of the cross-section PVA hydrogels with closed cells, (b) internally concave pores (IICPs), and (c) interconnected pores (ICPs). (d) Calculated local Poisson's ratio as a function of measurement area for PVA hydrogels with closed cells, IICPs, and ICPs. Modified and reproduced with permission from [49].

In addition to introducing auxeticity in hydrogels, research has been conducted to incorporate hydrogels into auxetic polymers to fabricate metamaterial composites with well-controlled swelling properties of hydrogels. A hydrogel composite developed by Bhullar and colleagues utilizes hydrogel particles made from acrylamide and 2-acrylamido-2-methyl-1-propanesulfonic acid, enclosed within an auxetic polytetrafluoroethylene (PTFE) jacket[69]. This PTFE jacket is renowned for its strong mechanical properties, such as high tensile strength and

resistance to fatigue, which are crucial for controlling how the hydrogel swells in water or saline. They used a commercially available microporous PTFE heat shrink tubing with a 5 mm diameter for the jacket. The PTFE's auxetic property, characterized by its negative Poisson's ratio, allows it to expand sideways when stretched, preventing excessive swelling caused by hydrogel particle size increase. This controlled expansion ensures consistent performance in aqueous environments, enhancing the stability and effectiveness of the composite material for biomedical applications. While the auxetic properties primarily derive from the PTFE jacket rather than the hydrogel itself, such composite materials hold promise for controlled swelling mechanisms of hydrogels in applications like regenerative therapies, including treating conditions such as intervertebral disc degeneration.

2.3 Geometric Transformation Mechanical Metamaterial

Geometric transformation mechanical metamaterials are engineered to undergo substantial shape changes in response to external stimuli[70, 71]. Hydrogels, unlike other materials, can respond to a broader range of stimuli, including environmental factors such as temperature, or light[72], enabling further advancements in applications, as summarized in Table 3. These transformations are immediate and are dictated by the specific design of the metamaterial's structure, rather than solely by the inherent properties of the materials used. This contrasts with four-dimensional (4D) printing hydrogels, which are programmed to change shape gradually over time in response to environmental factors[34, 73, 74]. These metamaterials employ geometrical patterns at the macro or microscale to achieve predefined mechanical responses. Applications of hydrogel-based geometric transformation mechanical metamaterials span fields such as soft robotics, tissue engineering, and biosensing[46, 47]. Their ability to undergo precise and controlled shape transformations makes them well-suited for environments where adaptability and reconfigurability are crucial.

Table 3. Geometric Transformation Mechanical Metamaterial

No.	Material	Stimuli	Study method	Fabrication method	Example application	Reference
1	N-isopropylacrylamide (NIPAM), N,N′-methylenebis(acrylamide), iron oxide nanoparticles	Laser light	Experiment and FEM simulation	Bulk polymerization	Tissue engineering, controlled drug release	46
2	NIPAM, acrylamide, 2-hydroxyethyl methacrylate (HEMA), polyethylene glycol diacrylate (PEGDA)	Temperature	Experiment and FEM simulation	Two-photon polymerization based 3D micro-printing	Information cryptology	47
3	N-isopropylacrylamide (NIPAM), 2-hydroxyethyl acrylate (HEA), N-acryloyltyramine (NATA)	Temperature	Experiment, mathematical and regression modelling, optical analysis, statistical analysis, and FEM simulation	UV photopolymerization	Molecular profiling	75

Reprogrammable shape transformations in composite hydrogel sheets were achieved by Guo and colleagues, leveraging hydrogel materials and mechanical metamaterial principles[46]. Their approach incorporates erasable and rewritable nanoparticle patterns, facilitating the material's adaptation to diverse shapes and functionalities. By integrating thermoresponsive poly(N-isopropylacrylamide) (NIPAM) with iron oxide nanoparticles (IONPs), the hydrogel sheet offers robust mechanical strength and thermal responsiveness. By designing specific IONP patterns within the hydrogel sheet, the researchers can control its shape changes (Figure 9a). The hydrogel sheet can change shape due to localized heating induced by light absorption in the IONP-patterned regions. When exposed to light, the IONPs heat up, causing the thermoresponsive

poly(NIPAM) to deform into different shapes as demonstrated experimentally and through FEM simulations (Figure 9b and c). This process allows for precise and reversible shape transformations, enabling dynamic reprogramming of the material's shape. With its adaptability, this material holds promise for applications in soft robotics, tissue engineering, and controlled drug release. The ability to rewrite nanoparticle patterns enhances its potential for adaptive geometric transformations, marking a significant advance in reprogrammable shape-changing materials and expanding avenues for innovative applications.

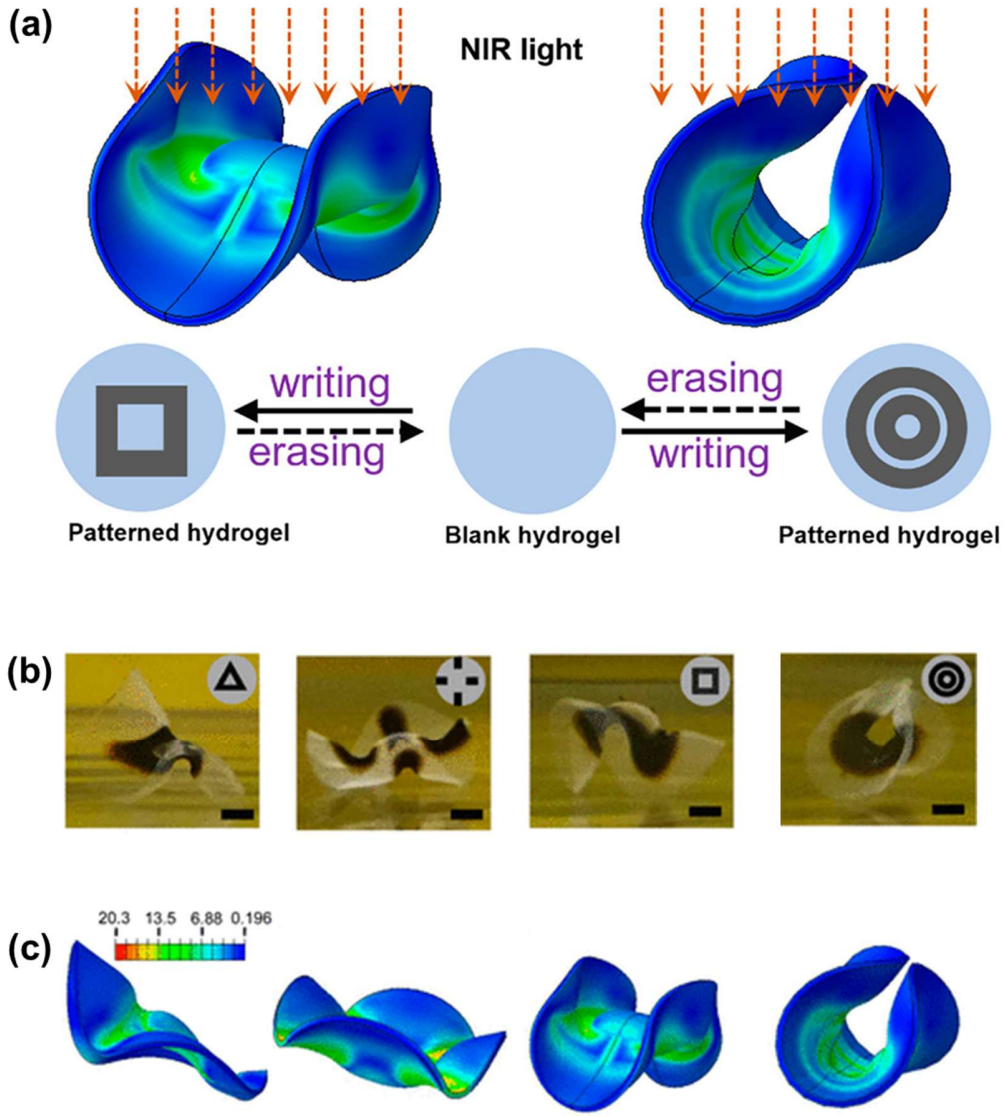

Figure 9. Reprogrammable shape-transformable composite hydrogel sheet utilizing erasable and rewritable nanoparticle patterns. (a) Schematic design of the shape-transformable composite hydrogel sheet achieved through near-infrared (NIR) light irradiation to modify nanoparticle patterns. (b) and (c) Experimental results and FEM simulations of shape transformations induced by laser irradiation, varying the shapes of the IONP patterns (black areas in the hydrogel design). The color legend denotes the stress distribution calculated by FEM in the sheet under laser irradiation. Modified and reproduced with permission from [46].

Apart from light stimuli, another geometric transformation potential has been explored by Zhang and colleagues which involve temperature variation[47]. They have developed a design approach that harnesses the geometric transformation via linearly responsive transparent hydrogels (LIHAM) to create reconfigurable micro-metastructures. The temperature-responsive nature of LIHAM hydrogel is governed by the use of NIPAM, acrylamide, HEMA monomers, and PEGDA crosslinker, which undergo reversible swelling and shrinking in response to temperature changes. This behavior facilitates precise control over the shape-changing process of embedded metastructures, allowing for dynamic reconfiguration in response to environmental stimuli. The design strategy leverages the hydrogel's tunable deformation properties, achieved through monomer concentration and weight ratio adjustments, to program the metastructures' geometric transformations. This design-driven approach enables wide-spectrum programmability, allowing for the encryption and display of complex information through thermal actuation, and enables the creation of reconfigurable micro-metastructures with dynamic geometric transformations. The material's ability to change shape in response to temperature changes has potential applications in various fields, including laboratory-on-a-chip technologies, microrobots, physically intelligent machines, and tuneable photonic devices.

The concept of geometric transformation is also highlighted in another study by Zhao and colleagues, which combines temperature changes and redox reactions to achieve pattern transformations in mechanical metamaterials upon hydrogel swelling[75]. They developed a hydrogel-based mechanical metamaterial utilizing a specially formulated hydrogel blend, combining NIPAM as the temperature-responsive monomer and N-acryloyltyramine (NATA) as the redox-responsive monomer. The material transforms between its breathing and buckling states

due to a critical transition, where stimuli-induced crosslinking increases stiffness and stress, causing rapid deformation (Figure 10a). NIPAM and NATA contribute to this transformation through their temperature-sensitive swelling and deswelling properties, enabling reversible changes that can be adjusted by varying monomer concentrations. The shape transformation is quantitatively evaluated by the deformation index (DI) upon swelling, which represents the shape deformation, particularly observing the rapid change at the critical transition point (Figure 10b). The critical transition point, where the geometry of the metamaterial undergoes significant transformation, depends on factors such as the shear modulus and the periodicity of the material (Figure 10c). The design uses mechanical metamaterial patterns to enhance this response, leading to noticeable geometric changes. This capability enables highly sensitive optical detection of biomolecules, surpassing conventional enzyme-linked immunosorbent assay (ELISA) by 10^3-fold and accurately predicting cancer prognosis. The innovation lies in exploiting mechanical metamaterial properties for nanoscale molecular analysis, paving the way for advanced materials capable of dynamically changing shape in response to biomolecular cues. This opens new possibilities in biosensing and beyond. The aforementioned works on hydrogel-based geometric transformation mechanical metamaterials demonstrate versatile applications beyond biomedical uses of hydrogels, stemming from the adaptability of these metamaterials. Particularly, the responsiveness characteristics of hydrogels play a crucial role in the mechanical metamaterial response and application development in this context.

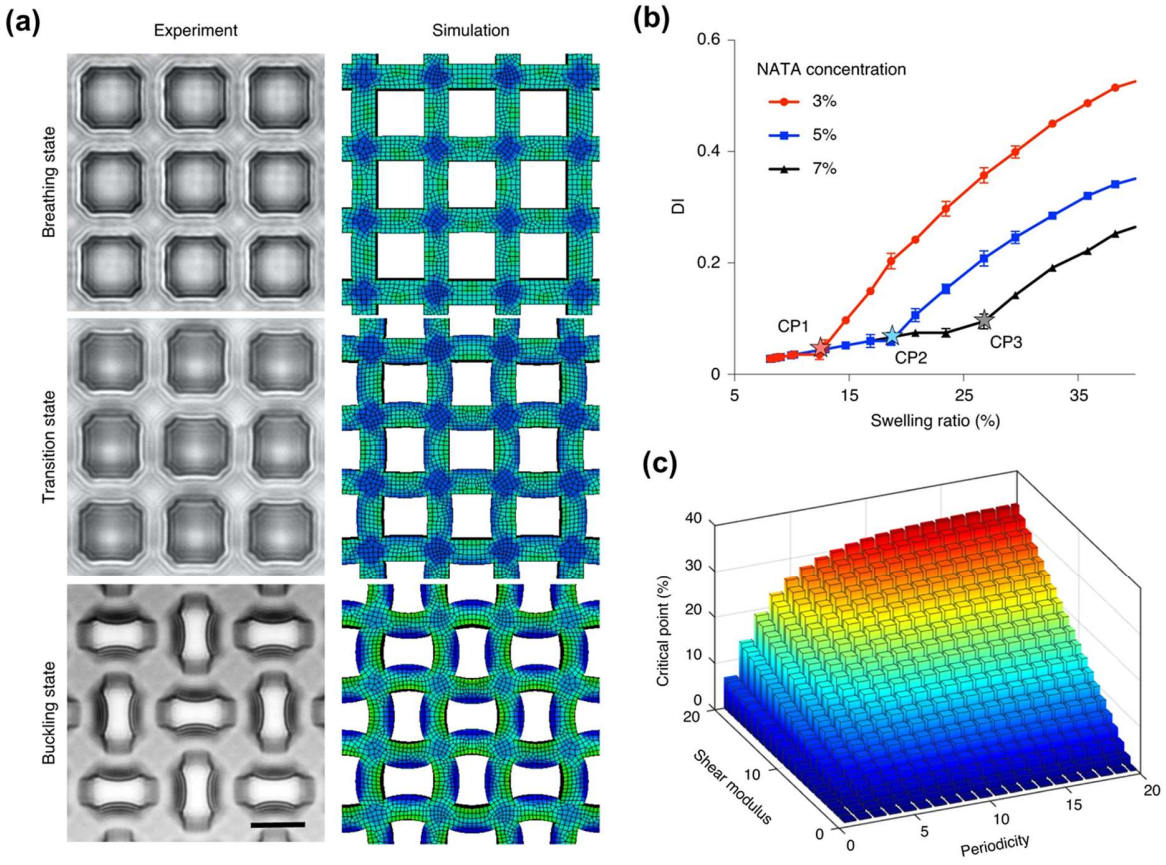

Figure 10. Hydrogel-based metamaterial with transitionable states. (a) Metamaterial deformation demonstrating the transitions between breathing, transition, and buckling states. (b) Deformation Index (DI) representing material deformation as a function of swelling ratio. (c) Theoretical modeling of critical points as a function of shear modulus and material periodicity. Modified and reproduced with permission from [75].

2.4 Programmable Mechanical Metamaterial

Programmable mechanical metamaterials are designed with the capability to adjust their mechanical properties in a controlled manner after fabrication, primarily through structural design

rather than inherent material properties[76, 77]. Leveraging the responsive characteristics of hydrogels, these programmable mechanical metamaterials can be altered or adjusted via external stimuli such as light, electric fields, or metal ions. The programmability of these materials enables dynamic adaptation to varying conditions, offering flexibility in applications ranging from biomedical devices and engineering materials to actuators[51, 54, 78]. In some instances, reprogrammability enhances their utility by facilitating repeated adjustments to their properties[50, 54]. For hydrogel-based programmable mechanical metamaterials, two key mechanical properties that are often programmed or reprogrammed are stiffness (Section 2.4.1) and toughness (Section 2.4.2), as summarized in Table 4.

Table 4. Summary of Programmable Mechanical Metamaterial

No.	Material	Key property	Study method	Fabrication method	Example application	Reference
1	Imidazolium perchlorate ($ImClO_4$), and PEGDA	Stiffness	Experiment and FEM	SLA 3D printing	Active electroacoustic or molecular ferroelectric metamaterials	50
2	Triphenylmethane leucohydroxide (TPMLH), o-nitrobenzaldehyde (NBA), acrylamide, N,N'-methylenebisacrylamide (MBAA)	Stiffness	Experiment and FEM	Bulk photopolymerization	Tunable underwater acoustic metamaterials	54
3	Acrylamide, acrylic acid, MBAA, ethylene glycol, Iron(III) chloride hexahydrate	Toughness	Experiment and Numerical modelling	DLP 3D printing	Engineering materials	51
4	Acrylamide, and alumina platelets	Toughness	Experiment	Bulk photopolymerization	Actuators and foldable structures	78
5	Acrylic acid, zirconium ions (Zr^{4+})	Toughness	Experiment	DLP 3D printing	Impact-absorbing elements	79

2.4.1 Stiffness-Programmable Mechanical Metamaterial

Hu and colleagues introduced stiffness-programmable mechanical metamaterials by fabricating a 3D-printed molecular ferroelectric hydrogel-based metamaterial using imidazolium perchlorate ($ImClO_4$)[50]. By employing electric-field-assisted additive manufacturing, they precisely fabricate intricate 3D geometries necessary for constructing ferroelectric crystalline lattices within PEGDA hydrogel scaffolds (Figure 11a). This approach incorporates $ImClO_4$ crystals into hydrogel-based printing, imparting the lattices with unique qualities such as self-healing and reprogrammable stiffness, contrasting conventional stereolithography (SLA) printing processes (Figure 11b). The precise 3D structure of the ferroelectric crystalline lattices, combined with the electrically adjustable properties of $ImClO_4$, allows the material to adapt its mechanical properties to different environmental conditions. These structures can dynamically adjust their mechanical response across various conditions due to the electromechanical properties of molecular ferroelectrics. For instance, the elastic modulus can increase by up to 25% as the electric field rises from 0 to 2 kV/cm (Figure 11c). This capability is promising for active electroacoustic metamaterials because they can automatically adapt to dynamic loads like vibrations and sound waves in response to electric fields, eliminating the need for complex machinery or manual adjustments.

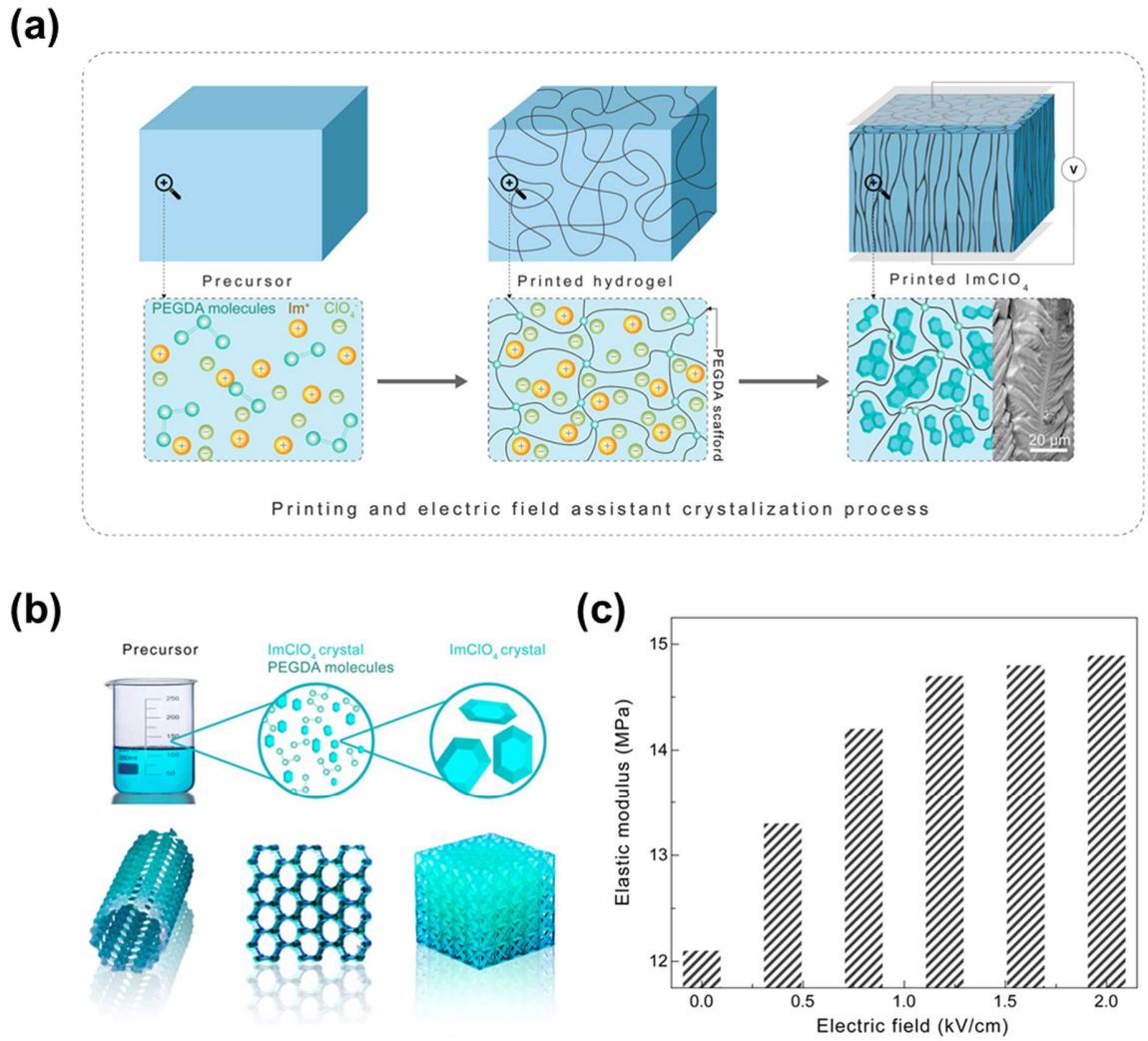

Figure 11. 3D-printed molecular ferroelectric metamaterial hydrogel. (a) Printing and electric field assistant crystallization process. (b) The conventional SLA printing process for ferroelectrics involves using a precursor formed by blending $ImClO_4$ powder with UV-sensitive resin. (c) Elastic modulus of the printed $ImClO_4$ as a function of the electric field. Modified and reproduced with permission from [50].

Aiming to develop a hydrogel-based metamaterial with reprogrammable stiffness and light-responsive characteristics, researchers engineered a mechanical metamaterial[54]. They utilized a light-responsive hydrogel to manipulate mass and stiffness ratios through bandgap tuning—specific frequency ranges where waves are blocked or reduced. They integrated triphenylmethane leucohydroxide (TPMLH) and o-nitrobenzaldehyde (NBA) into a polyacrylamide network, enabling the hydrogel to autonomously respond to light. This autonomous response allows the hydrogel to alter its structure, including its periodic arrangement, unit cell dimensions, and overall shape. These adjustments are crucial for fine-tuning the bandgap characteristics of the metamaterial, as the formation of bandgaps depends directly on its structure. Controlling bandgaps in light-responsive hydrogel metamaterials is essential for customizing wave manipulation and facilitating the reprogrammable adjustment of their functional capabilities, including mechanical properties. By adjusting the concentration of TPMLH and activating it with UV light, researchers can effectively reduce the Young's modulus of the hydrogel metamaterial from approximately 7.50 kPa before activation to around 4.72 kPa after activation. This modulation of mechanical properties directly influences the width and center frequency of the bandgaps, allowing precise control over which frequencies of waves are attenuated or transmitted through the metamaterial. The developed hydrogel-based metamaterial shows potential for applications requiring low impedance, such as biomedical devices and underwater acoustics, because it can effectively minimize signal loss and maximize transmission efficiency.

2.4.2 Toughness-Programmable Mechanical Metamaterial

Surjadi and colleagues have proposed a method for fabricating 3D-structured organohydrogels with tunable toughness, achieving energy absorption ranging from as low as 0.0035 to as high as 18.5 J g^{-1} using DLP 3D printing technology[51]. The organohydrogel formulation includes a photosensitive resin composed of acrylamide, acrylic acid monomers, and N,N'-methylenebisacrylamide (MBAA) crosslinker. After printing, the lattices undergo washing in water, immersion in an aqueous $FeCl_3$ solution, and treatment with ethylene glycol (EG) to produce metal-coordinated architected organohydrogels (Figure 12a). To enhance the structural integrity and dynamic mechanical properties of the hydrogel, dynamic metal coordination and hydrogen bonding are integral to its formulation. This involves incorporating specific ligands that interact with metal ions, such as Fe^{3+} from $FeCl_3$, within the polymer network to form reversible metal-ligand complexes. The unique 3D architecture of these organohydrogels allows for tailored adjustments in mechanical behavior, including energy absorption, density, and potentially stiffness, facilitated by precise control through 3D printing. This combination of advanced architecture and tailored molecular interactions contributes to their exceptional toughness (18.5 J/g), exceeding what traditional materials can achieve (Figure 12b). These advancements underscore the efficacy of mechanical metamaterial approaches in enhancing material performance across various engineering applications.

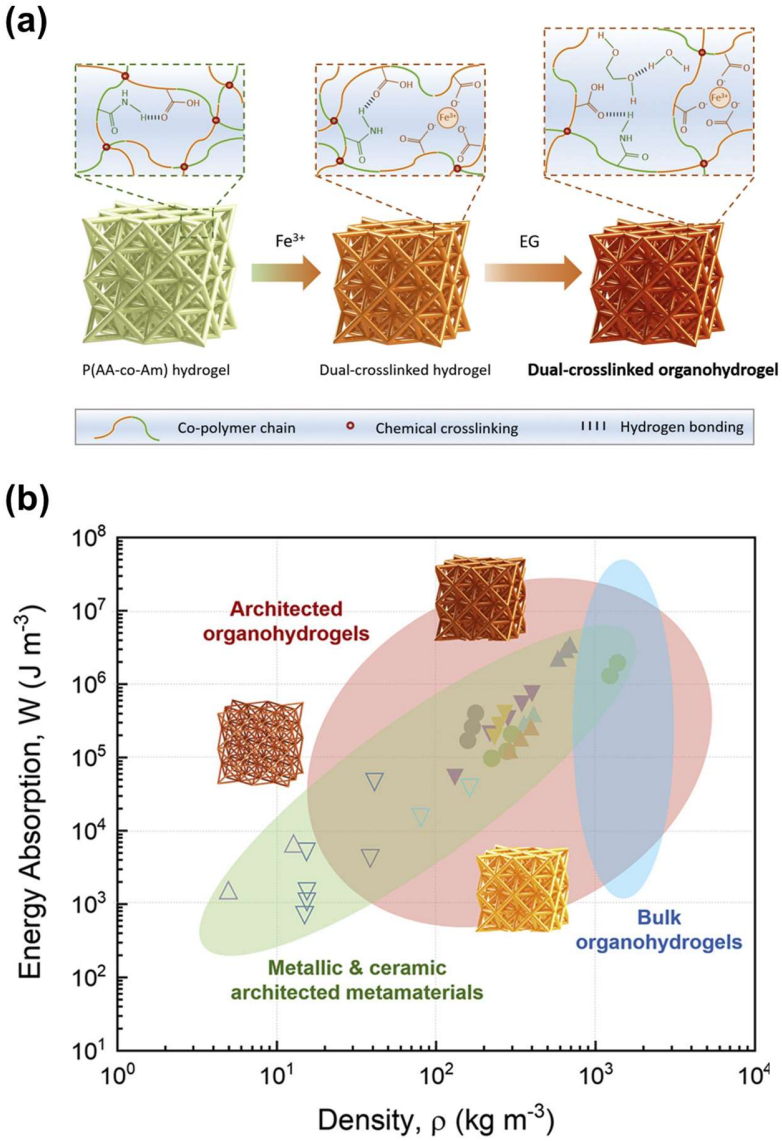

Figure 12. 3D-printed architected organohydrogels with ultra-tunable energy absorption. (a) Illustration of dual-crosslinked organohydrogel lattices, highlighting the formation of enhanced hydrogen bonds upon immersion of the metal-coordinated hydrogel in ethylene glycol (EG). (b) Comparison of mechanical properties of organohydrogels from this study and previous works. Modified and reproduced with permission from [51].

Mao and colleagues have developed a method to fabricate hydrogel-based composites with programmable fracture toughness by employing a "brick and mortar" structure[78]. This approach not only enables programmable fracture toughness but also achieves an overall high toughness value. This was achieved by incorporating alumina platelets into a polyacrylamide hydrogel matrix as the dispersion phase, enabling precise control over the material's mechanical behavior. By leveraging the reinforcing effect of these platelets and employing a straightforward hydration and dehydration process of the hydrogel matrix, the mechanical properties can be tuneable. This approach yields an impressive range of ultimate stress, spanning from 173 kPa to 102 MPa, and a Young's modulus ranging from 27.3 kPa to 3.5 GPa, thus offering versatility in design and application. Additionally, the material exhibits exceptional toughness, with fracture toughness reaching up to approximately 32,000 J/m². The high toughness is primarily attributed to energy dissipation zones, pull-out fracture modes, and complex crack paths, all facilitated by a unique "brick and mortar" structure, reminiscent of nacre, formed during manufacturing. The "brick and mortar" structure significantly enhances mechanical properties by effectively distributing stresses through aligned platelets, thereby improving toughness and strength beyond what the hydrogel matrix alone could achieve. This study highlights the material's versatility across diverse fields, with specific applications in actuators and foldable structures.

Apart from structural design, another tough metamaterial hydrogel was developed by Dong and colleagues through sophisticated architectures, utilizing supramolecules to form the precursor solution for 3D printing[79]. Their approach addresses common limitations in DLP printing of hydrogels, such as slow toughening and gelation processes. In their study, they utilize a precursor solution comprising acrylic acid, zirconium ions (Zr^{4+}), and the photoinitiator V-50. When exposed to digital light, this solution rapidly forms robust metallo-supramolecular hydrogels by facilitating

the *in situ* formation of carboxyl–Zr^{4+} coordination complexes (Figure 13a). These complexes act as physical crosslinks for poly(acrylic acid) chains, promoting rapid gelation through strong inter-chain bonding. This crosslinking process effectively stabilizes the hydrogel's structure, facilitating quick and efficient network formation under digital light exposure. It results in strong and robust crosslinks compared to traditional methods, enhancing the hydrogel's toughness and resistance to swelling. This integrated structural and mechanical enhancement can be considered another example of mechanical metamaterials. Furthermore, by controlling the grayscale of digital light during printing, they can encode structural gradients that induce swelling-driven morphing of the gel (Figure 13b). The obtained hydrogels achieve mechanical metamaterial characteristics through their engineered structures, which utilize controlled swelling-induced morphing and complex architectures to impart unconventional mechanical properties and functionalities beyond those of traditional hydrogel materials. Because of their outstanding mechanical properties, the printed hydrogels are showcased in proof-of-concept applications as impact-absorbing elements and high-sensitivity pressure sensors, underscoring their versatility across engineering and biomedical fields. This technique provides a promising approach to directly print robust hydrogels with customizable mechanical properties, including not only high toughness but also stiffness and resistance to swelling. Based on the above-mentioned works, while material composition remains fundamental for establishing and adjusting baseline properties suited to specific applications, the structural design approach inherent in programmable mechanical metamaterial hydrogels provides distinct advantages in customizing and augmenting mechanical functionality. This method allows for tailored mechanical behaviors without extensive alteration of chemical composition. By leveraging advanced fabrication techniques, structural design in mechanical metamaterials holds

promise in potentially overcoming limitations or constraints typically associated with the inherent properties of materials.

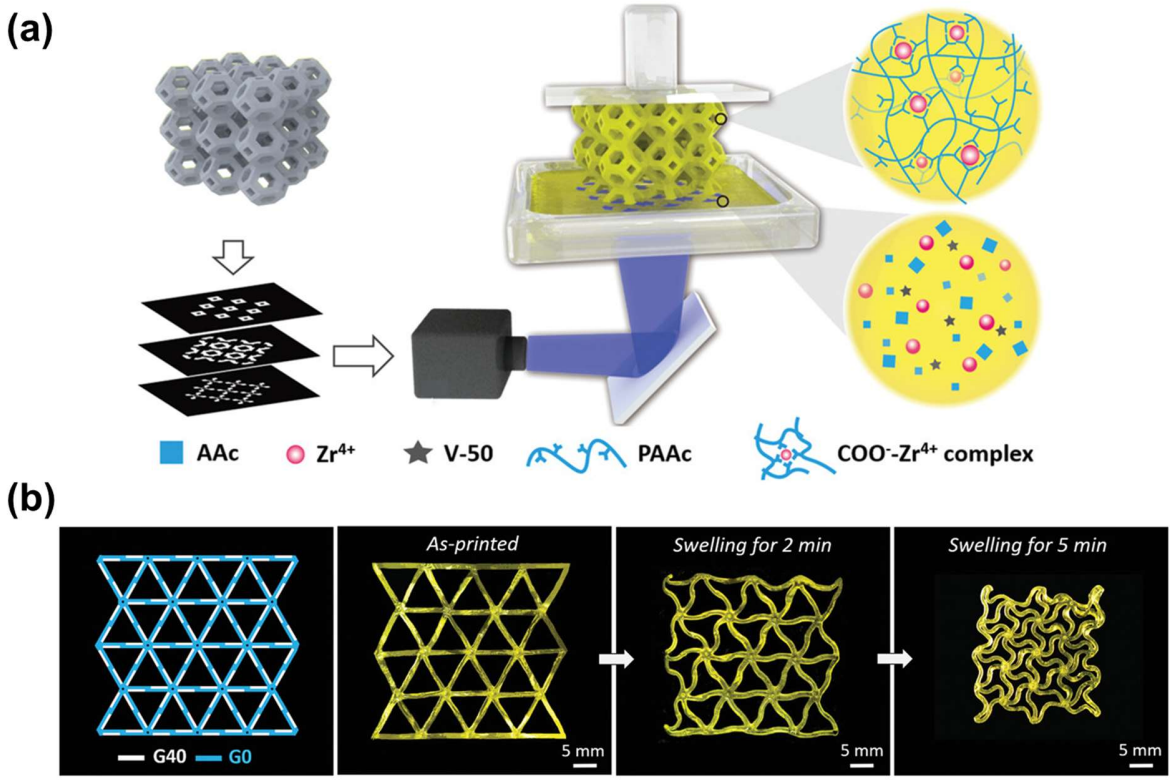

Figure 13. 3D-printed tough supramolecular hydrogels showcasing sophisticated architectures. (a) Schematic depicting the formation of tough supramolecular hydrogel via in situ carboxyl–Zr^{4+} coordination complexes as physical crosslinks within the gel matrix. (b) Demonstrated negative swelling behavior of the printed hydrogel lattice with in-plane gradients following incubation in the precursor solution. Modified and reproduced with permission from [79].

3. Current Challenges and Future Prospects

The developments in Sections 2.1 to 2.4 highlight various hydrogel-based mechanical metamaterials designed to achieve specific characteristics, including negative hydration expansion, auxetic behavior, geometric transformation, and programmable mechanical properties. Despite these advancements, several challenges and opportunities for further improvement in this field remain.

Structural Design:

In structural design, considerable attention is given to customizing macroscopic structures using techniques such as vat photopolymerization 3D printing, mold casting, or laser cutting. These enable robust control over mechanical behavior. However, the inherent softness of hydrogels presents challenges in achieving precise nanostructural designs[80, 81]. Advances in fabrication techniques tailored to hydrogels hold promise in overcoming these difficulties, potentially expanding metamaterial structural design possibilities to the nanoscale. Furthermore, exploring molecular-level arrangements offers opportunities to enhance the development of hydrogel-based mechanical metamaterials[49-51]. This ability to design at smaller scales enables enhanced control over the mechanical properties of hydrogels and paves the way for the creation of multi-scale mechanical metamaterials.

Biocompatibility:

Although several hydrogel-based mechanical metamaterials have been proposed, there have been few investigations into their biocompatibility, which is crucial for practical biomedical applications. Concerns about the biocompatibility of hydrogel-based mechanical metamaterials

stem from various factors. Many studies have explored multi-material systems consisting of hydrogels combined with other components like rubber or polymers. This may be the result of a limited biocompatibility of hydrogels with other material combinations and unresolved interfacial adhesion issues[82]. Additionally, the complex structural characteristics of mechanical metamaterials may further limit biocompatibility, even when using inherently biocompatible hydrogels[83, 84]. These intricate structures can create sharp edges, small pores, or confined spaces that hinder cell adhesion and growth, potentially leading to localized cell death or tissue damage. Addressing these challenges requires meticulous design and thorough testing to ensure that the obtained mechanical metamaterial is safe and effective for biological applications.

Multi-materials:

Due to the inherent softness of hydrogels, the use of single-material hydrogels poses challenges in providing structural integrity, which is detrimental to the functioning of biomedical devices. Consequently, various studies have integrated hydrogels with stiffer materials such as rubber and polymer to fabricate mechanical metamaterials[38-42]. This approach requires careful consideration of factors such as interfacial adhesion and fabrication complexities to ensure the multi-material systems are suitable for structural applications. Recent advancements in hydrogel research allow for multi-material printing, enabling seamless fabrication using two or more hydrogel components through techniques like bioprinting[30, 85]. However, future research should focus on exploring multi-material combinations, particularly utilizing various hydrogels for all components to enable the fabrication of high-structural-integrity mechanical metamaterials, thereby extending their potential applications.

Computational simulation:

Several studies on hydrogel-based mechanical metamaterials involve FEM simulations to aid in the design of mechanically responsive structures. However, FEM studies on hydrogels are typically less extensive compared to polymers or metals due to the complex mechanical behaviors exhibited by hydrogels, such as large deformation, time-dependent responses, and non-linear elasticity[86-88]. Moreover, mechanical metamaterials often display complex and unconventional mechanical behaviors, including auxetic behavior and unusual deformation patterns[89-91]. Modeling these behaviors accurately with FEM necessitates advanced constitutive models and numerical techniques capable of effectively capturing these complexities. Therefore, further advancements in computational simulation are crucial to enabling the design of more intricate structures and guiding experimental observations in hydrogel-based mechanical metamaterials. Recent advancements in AI-based metamaterial design[48] can be leveraged to overcome the limitations of design complexity in hydrogel materials.

Author Contributions

S.P. conceived the idea and developed the outline. S.P., Z.A.C, T.J.E.L, Y.T.C., E.L.L.N. and F.W. collected and analyzed data and drafted the manuscript. S.P., Z.A.C, and T.J.E.L compiled all sections and reorganized the writing with contributions from all authors. Z.A.C., E.L.L.N. and Y.T.C proofread the English. Y.T.C., E.L.L.N. and F.W. proofread the drafted manuscript.

Conflicts of interest

The authors declare that they have no conflict of interest.

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References

1. Jiao, P.; Mueller, J.; Raney, J. R.; Zheng, X.; Alavi, A. H., Mechanical Metamaterials and Beyond. *Nature Communications* **2023,** *14* (1), 6004.

2. Zadpoor, A. A., Mechanical Meta-Materials. *Materials Horizons* **2016,** *3* (5), 371.

3. Surjadi, J. U.; Gao, L.; Du, H.; Li, X.; Xiong, X.; Fang, N. X.; Lu, Y., Mechanical Metamaterials and Their Engineering Applications. *Advanced Engineering Materials* **2019,** *21* (3), 1800864.

4. Craster, R.; Guenneau, S.; Kadic, M.; Wegener, M., Mechanical Metamaterials. *Reports on Progress in Physics* **2023,** *86* (9), 094501.

5. Malakooti, S.; Doulah, A. B. M. S. u.; Ren, Y.; Kulkarni, V. N.; Soni, R. U.; Edlabadkar, V. A.; Zhang, R.; Vivod, S. L.; Sotiriou-Leventis, C.; Leventis, N.; Lu, H., Meta-Aerogels: Auxetic Shape-Memory Polyurethane Aerogels. *ACS Applied Polymer Materials* **2021,** *3* (11), 5727.

6. Zhou, X.; Ren, L.; Song, Z.; Li, G.; Zhang, J.; Li, B.; Wu, Q.; Li, W.; Ren, L.; Liu, Q., Advances in 3D/4D Printing of Mechanical Metamaterials: From Manufacturing to Applications. *Composites Part B: Engineering* **2023,** *254*, 110585.

7. Gao, J.; Cao, X.; Xiao, M.; Yang, Z.; Zhou, X.; Li, Y.; Gao, L.; Yan, W.; Rabczuk, T.; Mai, Y.-W., Rational Designs of Mechanical Metamaterials: Formulations, Architectures, Tessellations and Prospects. *Materials Science and Engineering: R: Reports* **2023,** *156*, 100755.

8. Ren, X.; Shen, J.; Ghaedizadeh, A.; Tian, H.; Min Xie, Y., Experiments and Parametric Studies on 3D Metallic Auxetic Metamaterials with Tuneable Mechanical Properties. *Smart Materials and Structures* **2015,** *24* (9), 095016.

9. Deng, B.; Xu, R.; Zhao, K.; Lu, Y.; Ganguli, S.; Cheng, G. J., Composite Bending-Dominated Hollow Nanolattices: A Stiff, Cyclable Mechanical Metamaterial. *Materials Today* **2018,** *21* (5), 467.

10. Veerabagu, U.; Palza, H.; Quero, F., Review: Auxetic Polymer-Based Mechanical Metamaterials for Biomedical Applications. *ACS Biomaterials Science & Engineering* **2022,** *8* (7), 2798.

11. Cui, S.; Gong, B.; Ding, Q.; Sun, Y.; Ren, F.; Liu, X.; Yan, Q.; Yang, H.; Wang, X.; Song, B., Mechanical Metamaterials Foams with Tunable Negative Poisson's Ratio for Enhanced Energy Absorption and Damage Resistance. *Materials* **2018,** *11* (10), 1869.

12. Dong, L.; King, W. P.; Raleigh, M.; Wadley, H. N. G., A Microfabrication Approach for Making Metallic Mechanical Metamaterials. *Materials & Design* **2018,** *160*, 147.

13. Lee, J.-H.; Singer, J. P.; Thomas, E. L., Micro-/Nanostructured Mechanical Metamaterials. *Advanced Materials* **2012,** *24* (36), 4782.

14. Bauer, J.; Meza, L. R.; Schaedler, T. A.; Schwaiger, R.; Zheng, X.; Valdevit, L., Nanolattices: An Emerging Class of Mechanical Metamaterials. *Advanced Materials* **2017,** *29* (40), 1701850.

15. Koetting, M. C.; Peters, J. T.; Steichen, S. D.; Peppas, N. A., Stimulus-Responsive Hydrogels: Theory, Modern Advances, and Applications. *Materials Science and Engineering: R: Reports* **2015,** *93*, 1.

16. Hendi, A.; Umair Hassan, M.; Elsherif, M.; Alqattan, B.; Park, S.; Yetisen, A. K.; Butt, H., Healthcare Applications of pH-Sensitive Hydrogel-Based Devices: A Review. *International Journal of Nanomedicine* **2020,** *15*, 3887.

17. Bayat, M. R.; Baghani, M., A Review on Swelling Theories of pH-Sensitive Hydrogels. *Journal of Intelligent Material Systems and Structures* **2021,** *32* (18-19), 2349.

18. Han, Z.; Zhang, J., Rapid-Responsive Hydrogel Actuators with Hierarchical Structures: Strategies and Applications. *ACS Applied Polymer Materials* **2023,** *5* (7), 4605.

19. Chen, J.; Peng, Q.; Peng, X.; Han, L.; Wang, X.; Wang, J.; Zeng, H., Recent Advances in Mechano-Responsive Hydrogels for Biomedical Applications. *ACS Applied Polymer Materials* **2020,** *2* (3), 1092.

20. Feng, W.; Wang, Z., Tailoring the Swelling-Shrinkable Behavior of Hydrogels for Biomedical Applications. *Advanced Science* **2023,** *10* (28), 2303326.

21. Jia, D.; Muthukumar, M., Theory of Charged Gels: Swelling, Elasticity, and Dynamics. *Gels* **2021,** *7* (2).

22. Mo, X.; Ouyang, L.; Xiong, Z.; Zhang, T., Advances in Digital Light Processing of Hydrogels. *Biomedical Materials* **2022,** *17* (4), 042002.

23. Lin, X.; Zhao, X.; Xu, C.; Wang, L.; Xia, Y., Progress in the Mechanical Enhancement of Hydrogels: Fabrication Strategies and Underlying Mechanisms. *Journal of Polymer Science* **2022,** *60* (17), 2525.

24. Xing, W.; Tang, Y., On Mechanical Properties of Nanocomposite Hydrogels: Searching for Superior Properties. *Nano Materials Science* **2022,** *4* (2), 83.

25. Wang, P.; Wu, M.; Li, R.; Cai, Z.; Zhang, H., Fabrication of a Double-Network Hydrogel Based on Carboxymethylated Curdlan/Polyacrylamide with Highly Mechanical Performance for Cartilage Repair. *ACS Applied Polymer Materials* **2021,** *3* (11), 5857.

26. Ding, H.; Dong, M.; Zheng, Q.; Wu, Z. L., Digital Light Processing 3D Printing of Hydrogels: A Minireview. *Molecular Systems Design & Engineering* **2022,** *7* (9), 1017.

27. Bao, Y.; Paunović, N.; Leroux, J.-C., Challenges and Opportunities in 3D Printing of Biodegradable Medical Devices by Emerging Photopolymerization Techniques. *Advanced Functional Materials* **2022,** *32* (15), 2109864.

28. Andreu, A.; Su, P.-C.; Kim, J.-H.; Ng, C. S.; Kim, S.; Kim, I.; Lee, J.; Noh, J.; Subramanian, A. S.; Yoon, Y.-J., 4D Printing Materials for Vat Photopolymerization. *Additive Manufacturing* **2021,** *44*, 102024.

29. Imrie, P.; Jin, J., Multimaterial Hydrogel 3D Printing. *Macromolecular Materials and Engineering* **2024,** *309* (2), 2300272.

30. Viola, M.; Piluso, S.; Groll, J.; Vermonden, T.; Malda, J.; Castilho, M., The Importance of Interfaces in Multi-Material Biofabricated Tissue Structures. *Advanced Healthcare Materials* **2021,** *10* (21), 2101021.

31. Kotsuchibashi, Y., Recent Advances in Multi-Temperature-Responsive Polymeric Materials. *Polymer Journal* **2020,** *52* (7), 681.

32. Boon-in, S.; Theerasilp, M.; Crespy, D., Temperature-Responsive Double-Network Cooling Hydrogels. *ACS Applied Polymer Materials* **2023,** *5* (4), 2562.

33. Kocak, G.; Tuncer, C.; Bütün, V., pH-Responsive Polymers. *Polymer Chemistry* **2017,** *8* (1), 144.

34. Pruksawan, S.; Lin, Z.; Lee, Y. L.; Chee, H. L.; Wang, F., 4D-Printed Hydrogel Actuators through Diffusion-Path Architecture Design. *ACS Applied Materials & Interfaces* **2023,** *15* (39), 46388.

35. Li, L.; Scheiger, J. M.; Levkin, P. A., Design and Applications of Photoresponsive Hydrogels. *Advanced Materials* **2019,** *31* (26), 1807333.

36. Pruksawan, S.; Chee, H. L.; Wang, Z.; Lee, Y. L.; Sivaraja, V. K. S. O.; Ow, S. Y.; Li, J.; Wang, F., Gold Nanorods Function as near-Infrared Light-Activated Microheaters for in Situ Curing of Injectable Hydrogel Therapies. *ACS Applied Polymer Materials* **2023,** *5* (6), 4565.

37. Kulkarni, R. V.; Biswanath, S. A., Electrically Responsive Smart Hydrogels in Drug Delivery: A Review. *Journal of Applied Biomaterials and Biomechanics* **2007,** *5* (3), 125.

38. Chen, Z.; Li, Y.; Li, Q. M., Hydrogel-Driven Origami Metamaterials for Tunable Swelling Behavior. *Materials & Design* **2021,** *207*, 109819.

39. Wei, Y.-L.; Yang, Q.-S.; Ma, L.-H.; Tao, R.; Shang, J.-J., Design and Analysis of 2D/3D Negative Hydration Expansion Metamaterial Driven by Hydrogel. *Materials & Design* **2020,** *196*, 109084.

40. Ma, L.-h.; Wei, T.; Rao, W.; Zhang, K.; Gao, H.; Chen, X.; Zhang, X.-c., 4D Printed Chiral Metamaterials with Negative Swelling Behavior. *Smart Materials and Structures* **2023,** *32* (1), 015014.

41. Tao, R.; Guo, Y.; Li, J.; Luo, J.; Yang, Q.; Chen, Y.; Wu, W., Expansion Mechanics of Hydrogel-Driven Metamaterials with Multiple Deformation Modes. *Giant* **2024,** *17*, 100243.

42. Ma, L.-H.; Wang, S.-D.; Liu, J.; Gao, H.; Zhou, W., The Design and Investigation of Hydrogel-Based Metamaterials with Ultra Large Negative Hygroscopic Expansion Ratio. *International Journal of Smart and Nano Materials* **2022,** *13* (1), 114.

43. Du, L.; Shi, W.; Gao, H.; Jia, H.; Zhang, Q.; Liu, M.; Xu, Y., Mechanically Programmable Composite Metamaterials with Switchable Positive/Negative Poisson's Ratio. *Advanced Functional Materials* **2024,** *34*, 2314123.

44. Skarsetz, O.; Slesarenko, V.; Walther, A., Programmable Auxeticity in Hydrogel Metamaterials Via Shape-Morphing Unit Cells. *Advanced Science* **2022,** *9* (23), 2201867.

45. Fozdar, D. Y.; Soman, P.; Lee, J. W.; Han, L.-H.; Chen, S., Three-Dimensional Polymer Constructs Exhibiting a Tunable Negative Poisson's Ratio. *Advanced Functional Materials* **2011,** *21* (14), 2712.

46. Guo, H.; Cheng, J.; Yang, K.; Demella, K.; Li, T.; Raghavan, S. R.; Nie, Z., Programming the Shape Transformation of a Composite Hydrogel Sheet Via Erasable and Rewritable Nanoparticle Patterns. *ACS Applied Materials & Interfaces* **2019,** *11* (45), 42654.

47. Zhang, M.; Pal, A.; Zheng, Z.; Gardi, G.; Yildiz, E.; Sitti, M., Hydrogel Muscles Powering Reconfigurable Micro-Metastructures with Wide-Spectrum Programmability. *Nature Materials* **2023,** *22* (10), 1243.

48. Tezsezen, E.; Yigci, D.; Ahmadpour, A.; Tasoglu, S., AI-Based Metamaterial Design. *ACS Applied Materials & Interfaces* **2024,** *16* (23), 29547.

49. Ma, Y.; Zheng, Y.; Meng, H.; Song, W.; Yao, X.; Lv, H., Heterogeneous Pva Hydrogels with Micro-Cells of Both Positive and Negative Poisson's Ratios. *Journal of the Mechanical Behavior of Biomedical Materials* **2013,** *23*, 22.

50. Hu, Y.; Guo, Z.; Ragonese, A.; Zhu, T.; Khuje, S.; Li, C.; Grossman, J. C.; Zhou, C.; Nouh, M.; Ren, S., A 3D-Printed Molecular Ferroelectric Metamaterial. *Proceedings of the National Academy of Sciences* **2020,** *117* (44), 27204.

51. Surjadi, J. U.; Zhou, Y.; Wang, T.; Yang, Y.; Kai, J.-j.; Lu, Y.; Wang, Z., 3d Architected Temperature-Tolerant Organohydrogels with Ultra-Tunable Energy Absorption. *iScience* **2021,** *24* (7), 102789.

52. Walker, E. L.; Wang, Z.; Neogi, A., Radio-Frequency Actuated Polymer-Based Phononic Meta-Materials for Control of Ultrasonic Waves. *NPG Asia Materials* **2017,** *9* (2), e350.

53. Zhang, K.; Ma, C.; He, Q.; Lin, S.; Chen, Y.; Zhang, Y.; Fang, N. X.; Zhao, X., Metagel with Broadband Tunable Acoustic Properties over Air–Water–Solid Ranges. *Advanced Functional Materials* **2019,** *29* (38), 1903699.

54. Patel, H.; Chen, J.; Hu, Y.; Erturk, A., Photo-Responsive Hydrogel-Based Re-Programmable Metamaterials. *Scientific Reports* **2022,** *12* (1), 13033.

55. Qiu, Y.; Ye, H.; Zhang, H.; Zheng, Y., Machine Learning-Driven Optimization Design of Hydrogel-Based Negative Hydration Expansion Metamaterials. *Computer-Aided Design* **2024,** *166*, 103631.

56. Curatolo, M., Effective Negative Swelling of Hydrogel-Solid Composites. *Extreme Mechanics Letters* **2018,** *25*, 46.

57. Zhang, H.; Guo, X.; Wu, J.; Fang, D.; Zhang, Y., Soft Mechanical Metamaterials with Unusual Swelling Behavior and Tunable Stress-Strain Curves. *Science Advances* **2018,** *4* (6), eaar8535.

58. Kolken, H. M. A.; Zadpoor, A. A., Auxetic Mechanical Metamaterials. *RSC Advances* **2017,** *7* (9), 5111.

59. Balan P, M.; Mertens A, J.; Bahubalendruni, M. V. A. R., Auxetic Mechanical Metamaterials and Their Futuristic Developments: A State-of-Art Review. *Materials Today Communications* **2023,** *34*, 105285.

60. Ren, X.; Das, R.; Tran, P.; Ngo, T. D.; Xie, Y. M., Auxetic Metamaterials and Structures: A Review. *Smart Materials and Structures* **2018,** *27* (2), 023001.

61. Wallbanks, M.; Khan, M. F.; Bodaghi, M.; Triantaphyllou, A.; Serjouei, A., On the Design Workflow of Auxetic Metamaterials for Structural Applications. *Smart Materials and Structures* **2022,** *31* (2), 023002.

62. Wang, S.; Guo, J.; Biczo, A.; Feng, N., Design and Macroscopic Mechanical Responses of Auxetic Metamaterials with Tunable Stiffness. *Materials & Design* **2024,** *241*, 112913.

63. Mizzi, L.; Salvati, E.; Spaggiari, A.; Tan, J.-C.; Korsunsky, A. M., Highly Stretchable Two-Dimensional Auxetic Metamaterial Sheets Fabricated Via Direct-Laser Cutting. *International Journal of Mechanical Sciences* **2020,** *167*, 105242.

64. Pruksawan, S.; Chee, H. L.; Wang, Z.; Luo, P.; Chong, Y. T.; Thitsartarn, W.; Wang, F., Toughened Hydrogels for 3D Printing of Soft Auxetic Structures. *Chemistry–An Asian Journal* **2022,** *17* (19), e202200677.

65. Bai, C.; Tang, A.; Zhao, S.; Liu, W., Flexible Nanocellulose/Poly(Ethylene Glycol) Diacrylate Hydrogels with Tunable Poisson's Ratios by Masking and Photocuring. *BioResources* **2020,** *15*, 3307.

66. Tsegay, F.; Hisham, M.; Elsherif, M.; Schiffer, A.; Butt, H., 3D Printing of pH Indicator Auxetic Hydrogel Skin Wound Dressing. *Molecules* **2023,** *28* (3).

67. Chansoria, P.; Blackwell, J.; Etter, E. L.; Bonacquisti, E. E.; Jasiewicz, N.; Neal, T.; Kamal, S. A.; Hoque, J.; Varghese, S.; Egan, T.; Nguyen, J., Rationally Designed Anisotropic and Auxetic Hydrogel Patches for Adaptation to Dynamic Organs. *Advanced Functional Materials* **2022,** *32* (43), 2207590.

68. Zhang, W.; Soman, P.; Meggs, K.; Qu, X.; Chen, S., Tuning the Poisson's Ratio of Biomaterials for Investigating Cellular Response. *Advanced Functional Materials* **2013,** *23* (25), 3226.

69. Bhullar, S. K.; Cerkez, I.; Sezer, A.; Jun, M. B. G., Swelling Behavior of Hydrogels within Auxetic Polytetrafluoroethylene Jacket. *Polymer-Plastics Technology and Engineering* **2015,** *54* (17), 1787.

70. Jiang, C.; Rist, F.; Wang, H.; Wallner, J.; Pottmann, H., Shape-Morphing Mechanical Metamaterials. *Computer-Aided Design* **2022,** *143*, 103146.

71. Wenz, F.; Schmidt, I.; Leichner, A.; Lichti, T.; Baumann, S.; Andrae, H.; Eberl, C., Designing Shape Morphing Behavior through Local Programming of Mechanical Metamaterials. *Advanced Materials* **2021,** *33* (37), 2008617.

72. El-Husseiny, H. M.; Mady, E. A.; El-Dakroury, W. A.; Zewail, M. B.; Noshy, M.; Abdelfatah, A. M.; Doghish, A. S., Smart/Stimuli-Responsive Hydrogels: State-of-the-Art Platforms for Bone Tissue Engineering. *Applied Materials Today* **2022,** *29*, 101560.

73. Imrie, P.; Jin, J., Polymer 4D Printing: Advanced Shape-Change and Beyond. *Journal of Polymer Science* **2022,** *60* (2), 149.

74. Imam, S. S.; Hussain, A.; Altamimi, M. A.; Alshehri, S., Four-Dimensional Printing for Hydrogel: Theoretical Concept, 4D Materials, Shape-Morphing Way, and Future Perspectives. *Polymers* **2021,** *13* (21).

75. Zhao, H.; Pan, S.; Natalia, A.; Wu, X.; Ong, C.-A. J.; Teo, M. C. C.; So, J. B. Y.; Shao, H., A Hydrogel-Based Mechanical Metamaterial for the Interferometric Profiling of Extracellular Vesicles in Patient Samples. *Nature Biomedical Engineering* **2023,** *7* (2), 135.

76. Lu, C.; Hsieh, M.; Huang, Z.; Zhang, C.; Lin, Y.; Shen, Q.; Chen, F.; Zhang, L., Architectural Design and Additive Manufacturing of Mechanical Metamaterials: A Review. *Engineering* **2022,** *17*, 44.

77. Montgomery, S. M.; Kuang, X.; Armstrong, C. D.; Qi, H. J., Recent Advances in Additive Manufacturing of Active Mechanical Metamaterials. *Current Opinion in Solid State and Materials Science* **2020,** *24* (5), 100869.

78. Mao, Z.; Huo, M.; Lyu, F.; Zhou, Y.; Bu, Y.; Wan, L.; Pan, L.; Pan, J.; Liu, H.; Lu, J., Nacre-Liked Material with Tough and Post-Tunable Mechanical Properties. *Journal of Materials Science & Technology* **2022,** *114*, 172.

79. Dong, M.; Han, Y.; Hao, X. P.; Yu, H. C.; Yin, J.; Du, M.; Zheng, Q.; Wu, Z. L., Digital Light Processing 3D Printing of Tough Supramolecular Hydrogels with Sophisticated Architectures as Impact-Absorption Elements. *Advanced Materials* **2022,** *34* (34), 2204333.

80. You, S.; Li, J.; Zhu, W.; Yu, C.; Mei, D.; Chen, S., Nanoscale 3D Printing of Hydrogels for Cellular Tissue Engineering. *Journal of Materials Chemistry B* **2018,** *6* (15), 2187.

81. Zhang, B.; Li, S.; Zhang, Z.; Meng, Z.; He, J.; Ramakrishna, S.; Zhang, C., Intelligent Biomaterials for Micro and Nanoscale 3d Printing. *Current Opinion in Biomedical Engineering* **2023,** *26*, 100454.

82. Naahidi, S.; Jafari, M.; Logan, M.; Wang, Y.; Yuan, Y.; Bae, H.; Dixon, B.; Chen, P., Biocompatibility of Hydrogel-Based Scaffolds for Tissue Engineering Applications. *Biotechnology Advances* **2017,** *35* (5), 530.

83. Saroia, J.; Yanen, W.; Wei, Q.; Zhang, K.; Lu, T.; Zhang, B., A Review on Biocompatibility Nature of Hydrogels with 3d Printing Techniques, Tissue Engineering Application and Its Future Prospective. *Bio-Design and Manufacturing* **2018,** *1* (4), 265.

84. Nasra, S.; Patel, M.; Shukla, H.; Bhatt, M.; Kumar, A., Functional Hydrogel-Based Wound Dressings: A Review on Biocompatibility and Therapeutic Efficacy. *Life Sciences* **2023,** *334*, 122232.

85. Wu, Y.; Su, H.; Li, M.; Xing, H., Digital Light Processing-Based Multi-Material Bioprinting: Processes, Applications, and Perspectives. *Journal of Biomedical Materials Research Part A* **2023,** *111* (4), 527.

86. Huang, R.; Zheng, S.; Liu, Z.; Ng, T. Y., Recent Advances of the Constitutive Models of Smart Materials — Hydrogels and Shape Memory Polymers. *International Journal of Applied Mechanics* **2020,** *12* (02), 2050014.

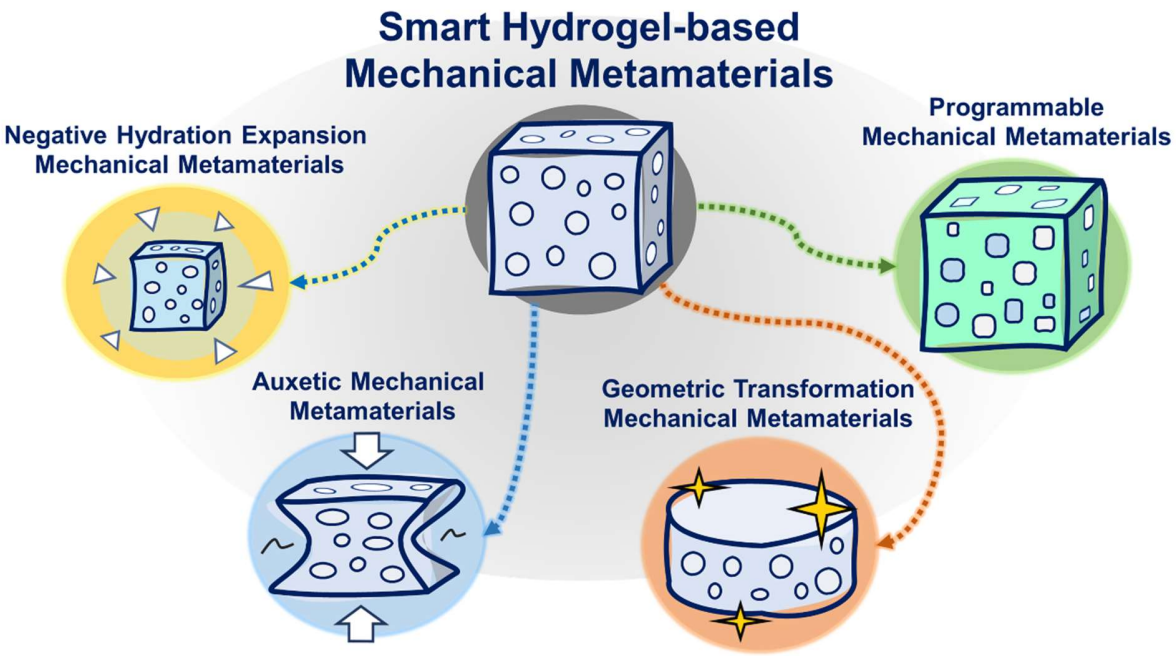
87. Lacroix, D.; Planell, J. A.; Prendergast, P. J., Computer-Aided Design and Finite-Element Modelling of Biomaterial Scaffolds for Bone Tissue Engineering. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **2009,** *367* (1895), 1993.

88. Liao, Q.; Kong, S.; Lin, L.; Tang, R.; Luo, Y.; Fu, S.; Liu, Y.; Li, H., The Application of Computer Simulation in Biomedical Hydrogels Research: A Review. *Journal of Molecular Liquids* **2024,** *394*, 123726.

89. Wu, W.; Hu, W.; Qian, G.; Liao, H.; Xu, X.; Berto, F., Mechanical Design and Multifunctional Applications of Chiral Mechanical Metamaterials: A Review. *Materials & Design* **2019,** *180*, 107950.

90. Barchiesi, E.; Spagnuolo, M.; Placidi, L., Mechanical Metamaterials: A State of the Art. *Mathematics and Mechanics of Solids* **2018,** *24* (1), 212.

91. Fan, J.; Zhang, L.; Wei, S.; Zhang, Z.; Choi, S.-K.; Song, B.; Shi, Y., A Review of Additive Manufacturing of Metamaterials and Developing Trends. *Materials Today* **2021,** *50*, 303.



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