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From Nature to Synthetic Systems: Shape Transformation in Soft Materials

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Abstract: Nature offers plethora of astonishing examples of shapes and functions from the aspects of both simplicity and complexity. The creation of synthetic systems that can morph in a controlled manner as seen in nature is of paramount importance in many fields of fundamental and applied sciences. The tremendous interest in self-shaping materials stems from a wide range of applications for these materials, ranging from biomedical devices to aircraft design. This review article highlights recent advances in understanding and designing thin, sheet-like soft materials that can transform into complex three-dimensional structures in a controlled manner by modulating the internal stresses. We review the general principles underlying shape transformation phenomena in natural and synthetic systems, and the significant achievements in fabricating self-shaping of soft materials via representative examples. We conclude with a discussion on the challenges facing the field, and future directions from the perspective of theoretical and experimental methodology and interdisciplinary applications.

1. Introduction

Nature is a perpetual source of inspiration for engineering functional materials. It is fascinating to observe how certain animals perform seemingly impossible tasks: efficiency of bird's flight, migration of whales across oceans, adaptation of penguins to harsh climates, and binding of gecko's feet to various surfaces etc. Self-organizing systems in nature ranging from micro-organisms to human beings exhibit variety of complex motions. In particular, shape transformation phenomena are ubiquitous in living systems such as plants, for example, curving of climbing plants around a pole, shaping of leaves at different stages of growth, and blooming of flowers. Such naturally occurring phenomena have triggered tremendous interest in understanding the transforming mechanism, as well as mimicking the structure-property relationship of living systems. It would be of immense scientific and economic value if we could employ self-shaping materials in artificial systems. For example, morphing aircraft wings with lightweight composites can enable shape transformation relative to the environment, thus dramatically improving aerodynamic efficiency.¹

Soft materials like elastomers and hydrogels exhibit a number of unique characteristics, including multifunctionality, biocompatibility, adaptability, low cost, and responsiveness to stimuli, and tunable strength and elastic modulus.^{2,3} They are not only ideal models for exploring natural phenomena such as shape transformation, but also promising components for synthesizing new materials that can acquire pre-programmed shape in response to stimuli.⁴ Although modulation of structural elements to induce simple bending, twisting and wrinkling has been reported earlier,^{5,6} programming materials to attain precise complex three-dimensional (3D) shapes was not explored until recently.^{7,8} It is interesting to note that the design principles of most synthetic systems can be traced back to natural systems like plants, seed pods, or functional organs of other animals like gecko's feet, butterfly wings etc., as illustrated in Figure 1.^{8,9,10,11,12,13,14,15} Such synthetic materials can find applications in drug delivery,¹⁶ tissue engineering,¹⁷ actuators,¹⁸ and soft robotics.¹⁹

The current review highlights recent advances in engineering complex 3D shape transforming (or self-shaping) soft materials by modulating the internal forces. We will limit our discussion to soft (thin, sheet-like) materials that deform readily, as opposed to bulky materials or materials

with very high elastic modulus, where residual stresses build up. Special emphasis is laid on the underlying mechanism of these transformation phenomena at different temporal and spatial transformations. First, we briefly describe the general principles underlying shape transformation of soft materials. We will then move on to describe recent key achievements in designing self-shaping materials. Finally, we will present the challenges and perspectives of this field. However, we have not included shape memory polymers as the principal mechanism in such materials is slightly different; this topic has been covered in depth in several excellent reviews.^{20,21}

2. Classification of Shape Transformation of Thin Sheets

Systems that undergo programmed shape transformation can be broadly classified based on the material architecture. Whenever two components (thin, sheet-like materials) that have different mechanical properties (i.e., volumetric expansion, change in stiffness) are coupled together, the final system attains a shape that will facilitate an equilibrium between its constituent elements.²² The class **I** system has simple distinct compartments of materials with specific characteristics of materials properties at an interface. Typical examples include bilayer polymer sheets (Figure 2a) and Figure (2a, b) represents two typical examples of this class of material architectures. The class **II** system comprises more than one materials that are amalgamated spatially to form complex vertical, lateral or programmed gradient patterns. This kind of spatial arrangement of materials is typically achieved by sophisticated fabrication techniques. Two representative systems are illustrated in Figure 2c,d.

In the following sections, we delve into details of these two groups of materials and different techniques that have been developed to achieve complex 3D shapes.²³ Except for the class **I** system that has distinct compartmentalization, it is a daunting task to define a unified model of these mechanisms. We, therefore, present the related modeling and simulation studies of these physical systems under each technique.

3. Shape Transformation of Class-I Thin Sheets

For the sake of clarity, we will start with a discussion on the simplest case, that is, the folding of simple, thin, sheet-like polymer bilayers to form 3D hierarchical structures. It is essential to

mention that these folding/rolling mechanisms not only mimic the movement of flora but they also pose a powerful platform for synthetic systems to form structures that are not commonly found in nature.²⁴ Examples from natural systems and corresponding synthetic systems are presented in each of the following sections. Due to its simplicity and versatility, this strategy has been used in designing materials for various medical applications, including controlled release of drugs and therapeutic agents, encapsulation of cells, microsurgery and microfluidics.^{25,26,27,28,29}

3.1. Programmed Folding of Bilayers.

Bilayers can be programmed to attain specific shapes by fine-tuning the mismatch between two layers. The inhomogeneity in volumetric change along the thickness is the primary driving force for bending in response to stimuli. The concept of using bilayer structures for forming definitive 3D structures has come a long way since the report by Hu *et al.*⁵ Some of the initial works in this field were derived from examples present in nature i.e., blooming of flowers or shaping of leaves¹³ and more recent studies have been aimed at modeling a physical system to mimic the “energy economy” of such naturally occurring phenomena. For example, the slender geometry of leaves and petals in flowers, have been observed to follow differential growth motif.³⁰ The midrib composite structure elongates longitudinally while the higher magnitude latitude expansion occurs in petals/sepals leading to wave cascade at the edges (Fig. 3a).³¹ When these systems grow differentially in a certain direction, in-plane stresses build up and they promote saddle like structures in petals and twisted helical structure in seed pods (Fig. 3b, 3c).³² The surface features found on dried apples and peas’ have helped us to understand the design criteria for core-shell materials with preferential surface properties and this can find applications such as drug carriers and self-cleaning surfaces.^{33,34}

Recently, Ionov *et al.* have pioneered the multi-step folding of isotropic stimuli-responsive polymer bilayers to fabricate complex 3D structures.^{24,35,36} The bilayer strips typically consists of a combination of active and passive layers made of thermoresponsive PNIPAm and poly-(methylmethacrylate) layers, respectively. The bilayers swell differentially when immersed in a solvent and lateral diffusion of water through the periphery triggers the folding. The key feature of such a process is the modulated hierarchical folding pattern. Since the diffusion activated region starts from the outer edge, by regulating the length, width, shape of pattern at the edges and the distance from the axisymmetric center, one can promote multi-step folding to achieve

complex shapes such as, pyramidal cones, multi-arm stars and tubular constructs (Figure 4).³⁷ By studying various design considerations for different shapes and the ‘minimal energy’ routes observed in experimental studies, they arrived at few important empirical rules for designing such stimuli-responsive materials.³⁸

Homogeneous and inhomogeneous (preferentially oriented to a certain direction) rolling of self-folding polymeric sheets have been studied extensively. Various analytical models and simulations using finite element analysis (FEA) have been proposed to predict the bending curvature, direction of rolling and the final shape, for a system with a specific configuration of thickness, initial stress and material elasticity.^{39,40,41} These self-folding materials have found applications in optics, drug delivery and tissue engineering.^{42,43,44}

3.2. Biomimetics

The exploration of *in vitro* biological shaping phenomena may lead to a new generation of biomaterials. In pursuit of mimicking nature, we are striving to integrate multiple functionalities harmoniously into individual synthetic systems. Tissues in our bodies communicate and coordinate over various spatial and temporal scales to produce seamless action.⁴⁵ It would be ideal to design a material with “target metric” made of cellular systems so that macroscopic dimensional changes can occur on demand as cells respond to environmental cues. However, configuring *in-vitro* systems to match that criterion is highly complex and challenging. In a very preliminary study towards this goal, experimentalists designed functional networks made of ensembles of picoliter (~65pL) lipid-coated aqueous droplets in oil.⁴⁶ A computer assisted droplet printer was synchronized to eject droplets into lipid-containing oil bath. These droplets were functionalized with membrane proteins to impart cohesive electrical responsiveness. The ensemble of droplets were stable, self-supported and exhibited elastic modulus in the range of 100-300Pa. To induce shape transformation of such droplet assembly, a gradient of osmolarity was created by joining layers of droplets with different osmolarity.⁴⁷ Capturing cells in these droplets in a way similar to micro-engineered cell-laden hydrogels could open up new routes for drug delivery and tissue engineering application.⁴⁸

Phospholipid vesicles of cell membranes can readily transform their shape in response to ambient conditions such as, pH, temperature, osmotic pressure etc.⁴⁹ In a recent report by Meeuwissen *et al.*, it was demonstrated that polymeric vesicles comprising of block copolymers

of poly(ethyleneglycol)-b-polystyrene exhibited controlled transformation into cup-like (stomatocyte) structures.¹¹ By tailoring the surface functional groups in such biomimetic materials, it is possible to achieve targeted drug delivery as they possess drug carrying capability.^{16,50}

4. Shape Transformation of Class-II Thin Sheets

In the previous section, we discussed how layered thin polymeric sheets (class I system) with distinct constituents can be programmed to attain specific shapes and the mechanism under such cases is fairly straight forward as seen from the illustrated examples. In the following section, we discuss class II of material architecture i.e., highly amalgamated heterogeneous systems.

4.1. Evolution of 3D Configurations from Non-equilibrium States

Recently, a combination of concepts such as differential geometry, Gaussian curvature, Lagrange strain tensor and target metric tensor have been employed to decipher equilibrium dynamics of mechanical instabilities and shape evolution in thin sheets.⁵¹ It is essential to develop theoretical models to fully harness the potential of shaping techniques but there are several challenges that make the modeling a difficult endeavor. For example, buckling is a localized bending phenomenon where a system lowers its elastic strain energy (e.g. in-plane compression) by assuming out-of-plane 3D configuration. There is a critical thickness up to which in-plane stretching is favored as opposed to 3D contour (buckling) and the complex interplay of these two forces across the spatial scale makes it tough to put together a comprehensive model.^{52,53}

Let us consider a thin sheet with no constraining boundary conditions, which constitutes an equilibrium state with zero residual stress. There may be several other geometrically equivalent shapes that suffice zero residual stress condition. If the thin sheet expands isotropically in response to external stimuli (i.e., heat, pH, ions, electromagnetic fields), the system can relieve its stress either by stretching radially or by acquiring contoured shape that initiate at certain points on the 2D surface. It is of utmost importance for us to locate origin points of these stresses and manipulate the stresses so as to achieve a desired shape by design. This is where the concept of non-Euclidean plates (NEP) becomes useful.^{7,54}

In short, non-Euclidean surfaces (plates) are those with non-planar 2D configurations and carry minimal elastic energy for a given material and configuration. This is particularly useful as there is no specific stress-free shape and we can utilize certain points (mid-surface) instead of a shape to represent equilibrium of the system.⁵² If the material expands symmetrically in radial direction (r) and isotropically in azimuthal direction by a factor $\eta(r)$ that is a function of radius, we can establish a link between those mid-surface points and a 2D metric tensor g (Figure 5). Here, the locus of mid-surface is expressed in polar coordinates (r, θ) and the equilibrium distance between points to be dl . When the material undergoes swelling or shape change, the equilibrium distances on these points change and now the metric tensor changes to \bar{g} . This defines the equilibrium distance between these points and the local strains more efficiently than macroscopic strain of the material (Equation 1).^{55,56,57}

$$dl^2 = dr^2 + r^2 d\theta^2; \quad g = \begin{pmatrix} 1 & 0 \\ 0 & r^2 \end{pmatrix}; \quad \bar{g} = \begin{pmatrix} 1 & 0 \\ 0 & r^2 \eta^2(r) \end{pmatrix} \quad (1)$$

When the material attains equilibrium state, it does so by relaxing its in-plane stress. The shape of the material is related to the Gaussian curvature (K) and local mean curvature (H) via local principle curvatures k_1 and k_2 [g,h]. The local metric coefficients (k_1, k_2) and their derivatives can yield growth characteristics and spatial outcome in a dynamic system (Equation 2).⁵²

$$H = \frac{1}{2}(k_1 + k_2); \quad K = -\frac{1}{\varphi} \frac{\partial^2 \varphi}{\partial x^2} \quad (2)$$

To illustrate this growth driven by instability, let us consider an example of tearing of a large plastic sheet (Figure 6a).⁵⁸ In this case, one can notice both elastic stretching of the material along the azimuthal direction and plastic deformation at the edges where it is least restricted.⁵⁹ But the characteristic aspect of such phenomena would be the appearance of fractal-like of wavy patterns along the edges, as a result of the interplay between stretching and bending. The wavelength (λ) of such a pattern varies as X^m , where X is the distance from the axial center to the point of interest and m is a numerical constant that is related to the direction of expansion.⁴³ The consequent Gaussian curvature would explain the reason behind such formation in naturally occurring phenomena such as a suspended curtain (Figure 6b). In living systems like cabbage, the fractal-like shaping is driven by differential growth and dehydration (Figure 6c).⁶⁰

4.2. Multiple Roads to the Same Destination

The shaping mechanism in the case of Class II systems becomes vastly complex as the need to create stable force gradients arise. Such “energy gradients” needed for shaping in the heterogeneous system can be created by numerous pathways such as, differential swelling or shrinkage, local change in chemistry or cross-linking density, changes in the solvent pH, photoisomerization or photothermal heating, morphological instability and residual in-plane/out-of-plane stress.^{51,61,62,42} Towards this end, multiple techniques have been developed to achieve controlled shaping of class II systems, namely, small-scale modulation of internal stresses, dissimilar crosslinking of polymers either by chemical changes or soft lithography,⁶³ inclusion of heating elements,⁶⁴ origami,^{65,66} and ionoprinting.¹⁰ In the following sections, we discuss these techniques in detail highlighting the peculiarities, advantages and potential applications.

4.2.1. Differential Crosslinking

The creation of defined “energy gradients” within materials is challenging. One of the first demonstrations was recently reported by Klein *et al.*⁷ The integrated “non-Euclidean target metrics” within a 2D polymer sheet could lead to programmable shape formation by minimizing the local energy within the sheet. In this work, thermoresponsive poly(N-isopropylacrylamide (PNIPAm)) hydrogel disks with radial density gradient of polymer networks was synthesized by controlling the monomer concentration via soft lithography approach.⁶³ The difference in polymer density dictates the preferential localized swelling of the hydrogel disks. PNIPAm exhibits a distinctive lower critical solution temperature (LCST) of 33°C. The team succeeded in configuring precise shapes that matched the calculated target metric tensors ranging from $\bar{K} > 0$, $\bar{K} < 0$ and the values in between (Figure 7a-7d). However, it is important to note that this is true for free standing NEP's and when the system is thin and constrained, wrinkling is the dominant mechanism to eliminate in-plane stress.^{7,67} This strategy, however, suffers from incapability of fabricating complex patterns and limited resolution of patterns. This technique is only applicable to polymer sheets within a specific range of thickness and bending modulus. As the thickness of the sheet enlarges, Gaussian curvature at ‘target metrics’ gets limited.⁶⁸

4.2.2. Halftone Lithography

As we mentioned earlier, generating stress gradient locally in a material is required to shape the system. Since residually stressed systems do not have a specific stress-free configuration, it is difficult to map the evolution towards their final 3D shape from their initial non-equilibrium state.⁵⁴ Few key questions are still unresolved, namely, what dictates the spatial coordinates of a system at which in-plane stress mitigates to produce 3D shapes? And why certain configurations wrinkle even though they have negative Gaussian curvature, which is contradictory to the Gaussian framework established for NEPs. Towards this direction, many groups have made attempts to elucidate both theoretical underpinnings and experimental designs.^{63,69}

One such example has been reported by Kim *et al.*⁶³ In this work, a “halftone gel lithography” approach was developed to precisely control the ‘target metric’ points (magnitude and positioning) on photo-crosslinkable PNIPAm and benzophenone acrylamide (BPAm) copolymer films. The unique aspect of this strategy is the smooth gradient of cross-linked regions that enables us to form truly arbitrary shapes like Enneper’s minimal surfaces, in contrast to conventional linear configuration systems.⁷⁰ Briefly, precursors of polymers were subjected to tuned ultraviolet light (~360nm) in a spatially controlled manner to create alternating pattern of high and low crosslinking density. The localized crosslinking density of polymers dictates the regional differential in swelling of the thin film. By carefully calibrating the distance between and the diameter of the crosslinked regions, material was approximated to be homogeneous in terms of elasticity and swelling was set to vary from $\Omega_{\text{low}}=2.3$ to $\Omega_{\text{high}}=8.2$ (swelling Ω , is a ratio of homogeneous area of the thin film in neutral solvent to dry state) . As shown in the image (Figure 9), various pattern of target metrics can be designed in this process and subsequently induce the formation of complex geometric structures that comply with the Gaussian curvature calculation.

Although this work is a positive improvisation over previous reports, there are certain limitations such as restricted thickness/elasticity of the material and the difficulty of configuring geometrical shapes where local maxima of Gaussian curvatures superimpose. Under such cases, complex play of opposing in-plane stresses, bending and wrinkling forces might hinder our ability to predict the final shape of the material.

As opposed to the simple bending in polymer bilayers, modeling the shaping behavior of class II systems is highly complex. The analytical treatment provided for halftone lithography paves a method to model heterogeneous systems with asymmetrical ‘target metrics’ and hence unique shapes.^{15,68}

4.2.3. Small-Scale Modulation of Stresses

Another strategy of positioning ‘target metrics’ relies on the clever geometrical arrangement of multiple components with slight change in their mechanical properties. Such an arrangement would lead to a steady gradient along the locus.⁷¹ Recently, Wu *et al.*⁸ demonstrated an advanced level of fine tuning the shape transformation of 2D sheets into precise cylindrical and conical helices (Figure 9a). Helices are structures of significance, ranging from DNA double helix, many seed pods and to climbing plants in nature, as they represent one of the most stable, energetically efficient configurations of packing.^{12,72} The crucial criteria of design involves the small-scale modulation of lateral internal stresses by integrating multi-components with large mismatch of swelling/shrinkage ratios and elastic moduli within thin sheets (Figure 9a). To achieve inhomogeneous swelling/shrinkage, 2D sheets with alternating strips of PNIPAm and PNIPAm/poly(2-acrylamido-2-methylpropane sulphonic acid (PAMPS)) were created by photopatterning approach.⁸ PNIPAm undergoes severe volumetric transition (~90%-150%) when heated to temperatures above its LCST or upon incubation with ionic solvents. The combination of PNIPAm and PAMPS enables the modulation of the regional differential in swelling/shrinkage and mechanical properties of the patterned gel sheets. Upon the change in temperature or ionic strength of the solvent media, the gel sheets underwent pre-programmed shape transformation to acquire helical or conic shapes.⁸

It is interesting to note that sole in-plane stretching is sufficient to drive the shape change behavior. More compact helices were formed at lower values of θ and for a specific angle ($\theta = 45^\circ$), normalized chirality of left-handed or right-handed helix was equally probable (Figure 9b). The number of turns in the helix and the pitch of these turns were dependent on the elastic modulus and gradient stress tensor within the gel strips, which is determined by the spatial composition of hydrogel and the properties (i.e., ionic strength) of solvent media. A drastic change in elastic modulus (E) and volume phase transition was found highest at 1.2 to 1.7 M of

NaCl in water for a given composition of the polymer strip. By varying the geometric parameters of these gel strips, the radii of curvature of the helix can be regulated, and new design such as conical helices can be created as predicted.^{73,32} The same strategy of small-scale modulation was employed to achieve continuous reversible transformations of thin composite sheets from planar configuration to 3D arcs, to tubes, and to helices, in response to stimuli such as temperature and pH (Figure 9c).

Although small-scale modulation in a planar system is an effective tool to control the evolution of 3D shapes, it is still limited in its scope, as the volumetric phase change in polymers (i.e., PNIPAm and PAMPS) is strongly dependent on the diffusion rate of ions inward/outward the polymer networks. The actuation time for shape transformation process usually takes several hours depending on the solvent/polymer combination, which could be a bottleneck point for their use in applications that demands rapid actuation.⁷⁴

4.2.4. Ionoprinting via Electrochemical Electrodes

The dendritic structure found in plants and in leaves (i.e., halves of leaves attaching to cellulosic backbone) serves two different purposes: i) transport of water and nutrients; and ii) modulation of the growth of a plant by maximizing its efficiency in capturing solar energy.^{75,76,30} In a similar way, one can make use of the transport nature of polymer matrix to pattern structures that will guide the shaping mechanism (Figure 10a).

Palleau *et al.*¹⁰ developed a unique technique ('ionoprinting') for fabricating complex 3D shapes via consequential transformation in a controllable yet reversible manner. Instead of crosslinking the polymer or changing the concentration of monomer, ions are directionally and locally injected into the material via electrochemical electrode (voltage > 5V) to induce localized crosslinking and hence stresses. The ion flux can be controlled effectively by moderating the current passing through the electrode (Figure 10b).

The ions from the electrode diffuse into the polymer networks and bind to the oxygen-rich molecular moieties to form chelation complexes. The ion-binding event induces localized stresses that actuate the macroscopic shape formation of the gel. This transformation can be further complemented by immersing the material in a solvent that induces differential stresses

due to osmotic pressure. One can control the shape and configurable pattern by regulating the ion concentration, pattern density, solvent type and time of immersion in a solvent. Such controllable deformation is rapid (~ 10 s). However, the limiting factor for this strategy might be the relatively low resolution of patterning, and possibly a narrow range of polymers and electrode combination that can be selected for ionoprinting.

4.2.5. Electronically Programmable 3D Hydrogels

The “snapping” action of the Venus flytrap is one of the most fascinating phenomena among plants. The fast response ($<$ millisecond) is attributed to the rapid transport of action potential from the trigger hairs and snap-buckling instability. Gleaned from such phenomena, researchers have developed a concept that employs electronically actuated network that acts as a locus of deformation in soft materials.^{13,77}

Built upon the innovative design of electronically deployable balloon stents for treating vascular diseases, researchers have devised a new way to control the shape transformation of soft materials.^{78,79} The method involves embedding ultra-flexible network of thin mesh wires that act as joule heating elements in a PNIPAm hydrogel matrix (Figure 11).⁸⁰ This electronically activated network of microheaters provides a highly controllable method to rapidly raise the temperature of the matrix beyond LCST ($>40^\circ\text{C}$) in a time scale (130 s) that is comparable to the immersion of the matrix in hot water (45 s), without affecting the stiffness of the hydrogel matrix. Application of voltage (~ 5 V) through an externally controlled circuit results in joule heating output of 0.327W, thus leading to 35% shrinkage in the combined hydrogel and mesh matrix. One can obtain zero Gaussian curvature or smooth ‘target metric’ by adjusting the spatial electrode density, heating sequence of the electrode, and the thickness of hydrogel. Such shrinkage induced by joule heating can be reversed by simply placing the hydrogel in cold water or by turning off the heating elements connected to microheaters. Heterogeneous swelling can be achieved by clever geometrical arrangement of heating elements and selectively switching on/off the electrode (Figure 11). The advantage of including such conductive networks in soft materials is that one can program the materials to stretch or bend without losing the functionality. This strategy is very attractive for applications in such as soft robotics,⁸¹ *in vivo* diagnostics,^{82,83} optical waveguides and wireless optogenetic devices.⁸⁴

4.2.6. Inclusion of Inorganic Nanomaterials to Induce Shaping

The integration of inorganic nanomaterials (i.e., carbon nanotubes and graphene sheets) with soft materials can be used to generate novel functional hybrids with shape transformation characteristics.⁸⁵ For example, single wall carbon nanotubes (SWNTs) with intriguing mechanical stability, photothermal and conducting abilities, can be used to drive the shaping mechanism. In a recent report by Zhang *et al.*, SWNT-PNIPAm strips of specific dimensions were embedded in thin low-density polyethylene sheets as hinges.⁸⁶ The exposure of such sheets to near-infrared (NIR) light triggered the dehydration of neighboring PNIPAm region, and hence the subsequent actuation to form cubic boxes, due to localized heating arising from the conversion of light to heat by SWNT (Figure 12a).

Inclusion of reduced graphene sheets (rGO) into thermally responsive, protein-based peptide hydrogels could also result in synergistic macroscopic shape changes.⁸⁷ Wang *et al.* exploited the shape transformation of anisotropic microstructures made from elastin-like hydrogel networks embedded with peptide functionalized rGO (Figure 12b).⁹ The system exhibited dual-mode actuation by curling due to the ability of converting absorbed NIR light to thermal heating by rGO sheets. The actuation and reversal time for a full range of motion was in the order of 3-10 s. The reversal was up to 80% for almost 100 cycles. Since biological fluids and tissues show maximum transparency to infrared radiation, this concept could open up new territory for remotely controlled cell-culture scaffolds and such rational combination of 1D or 2D carbon forms with electroactive polymer systems can find potential applications in robotic actuators, artificial muscles, and drug delivery systems.^{88,89,90}

Inclusion of inorganic elements enables tailoring the system to respond to different stimuli. Photoresponsive materials containing azobenzene have been thoroughly researched.⁹¹ The integration of photothermal agents (i.e., gold nanoparticles and graphene sheets) in a thermoresponsive polymer (i.e., PNIPAm) imparts the composite with shape transforming capability in response to light with predetermined wavelength particularly near-infrared range. These nanocomposites can be used for remotely controlled delivery of biological agents as a result of shape change.⁹² In a similar way, one can introduce inorganic elements that are

responsive to electric and magnetic fields to drive the shaping of materials, hence enabling their applications in molecular separation, controlled drug delivery and mechanical actuators.^{93,94}

5. Conclusions and Future Perspectives

Recently, the design of shape transforming soft materials has become a blooming exciting field, as discussed in this review. Despite the fascinating progress in the past five years, there remain several challenges that require interdisciplinary efforts from chemists, mathematicians, materials scientists, nanotechnologists, biologists, and engineers. Research on this promising field is expected to evolve in several directions.

First of all, theoretical modelling needs to be evolved to quantitatively predict or interpret the correlation between material designs to the dynamic transformation and final morphology of materials, as the complexity of the researched systems will continue to increase. Precise control over the target metric in shapes other than planar is yet to be realized.

Secondly, new experimental methodologies have to be developed for better control over the integration of different compositional elements on different length scales (particularly at nanoscale), as well as for in-situ characterization of the temporal and spatial variations in mechanical properties of the materials with appropriate resolution. The current characterization techniques cannot fetch real-time data of dynamic and cooperative signaling between components, in a non-invasive manner. Moreover, the rapidly rising demand for shape transforming materials will continuously urge one to consider the following aspects:

- New strategies to achieve complex geometries by imparting multi-stimuli responsiveness to materials during the hierarchical design process. Recent report by Thérien-Aubin *et al.* demonstrated a two-step shape-transforming process by integrating polymers that are responsive to two different temperatures. As we increase number of acting stimuli, the complexity of design increases exponentially.
- Totally radical concepts for programming structures that can take arbitrary shapes on demand. Current advances in polymer/inorganic hybrid materials enable us to remotely-trigger the shape transformation of materials. Although the existing strategies largely rely on localized patterning of responsive regions, the appropriate design of sequential

exposure or shaping of light resource may offer new approaches to fabricate structures that can morph into arbitrary shapes on demand without the limits of pre-patterning.

Third, most of the applications of shape transforming materials are still in their conceptual stage and new applications demand knowledge of diverse fields such as nanoscale fabrication, mathematical modeling, chemical synthesis, etc. In conclusion, shape transforming soft materials carve a niche of their encompassing various fields of research and play a crucial a role as we step into greener and more sustainable future.

Figure 1.

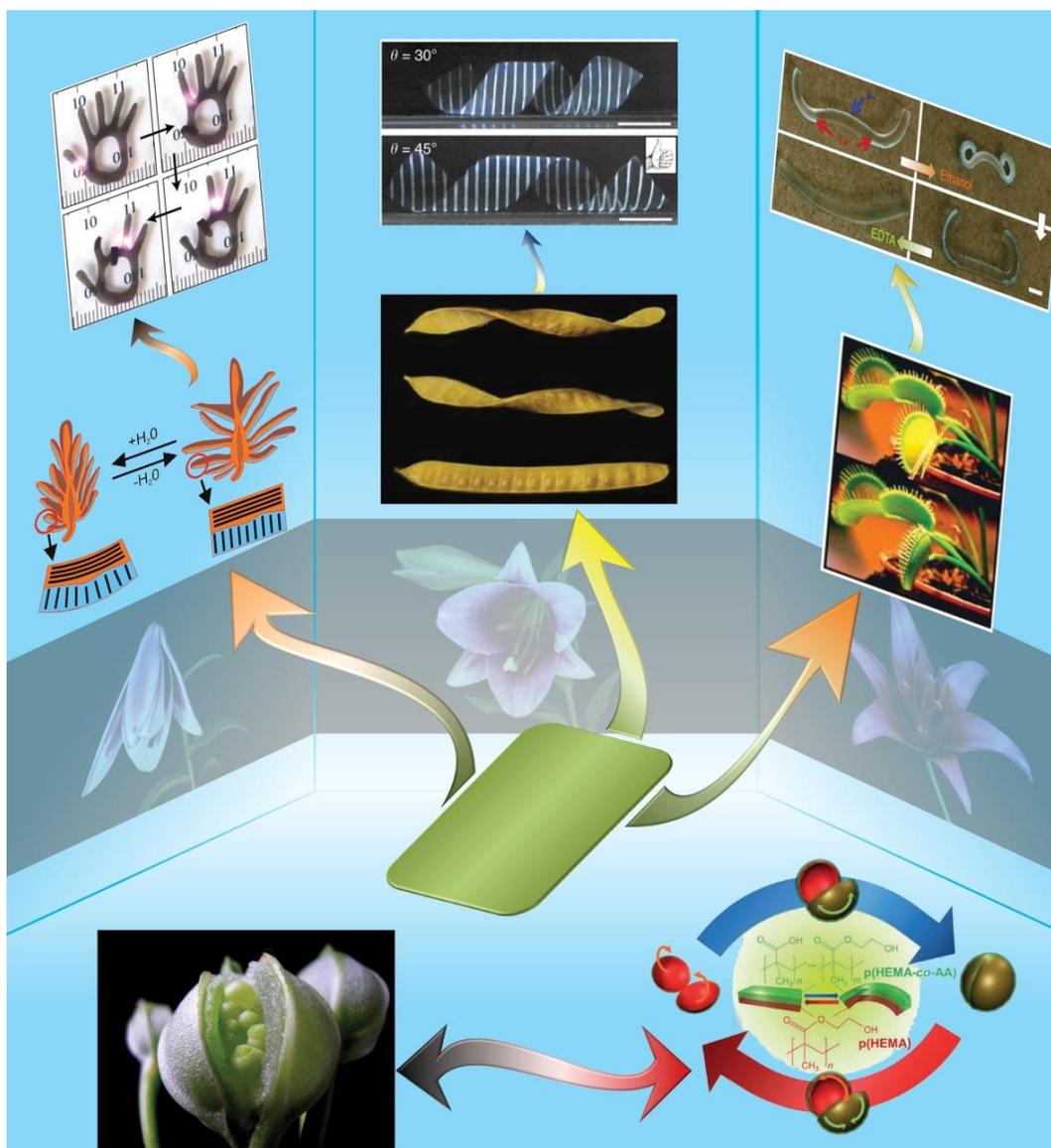


Figure 1. A schematic diagram illustrating the advancement of different shapes in synthetic systems from a plane, thin sheet-like material. In these cases, corresponding examples of natural systems have been highlighted.

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Figure 2.

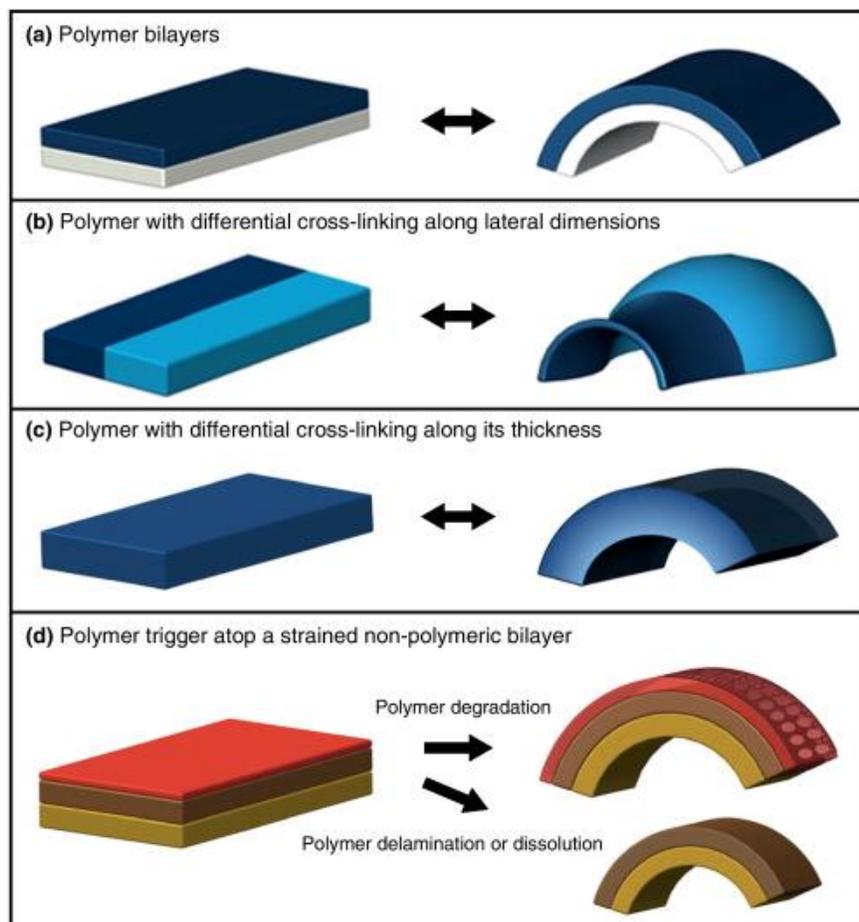


Figure 2. (Top to bottom) Representative examples of categorization in self-folding thin film like materials. Inset **a** and **b** represents class one i.e., systems that have distinct interface. Inset **c** and **d** represents class two systems that have gradient type amalgamation of materials with different properties or gradient in vertical or lateral directions.

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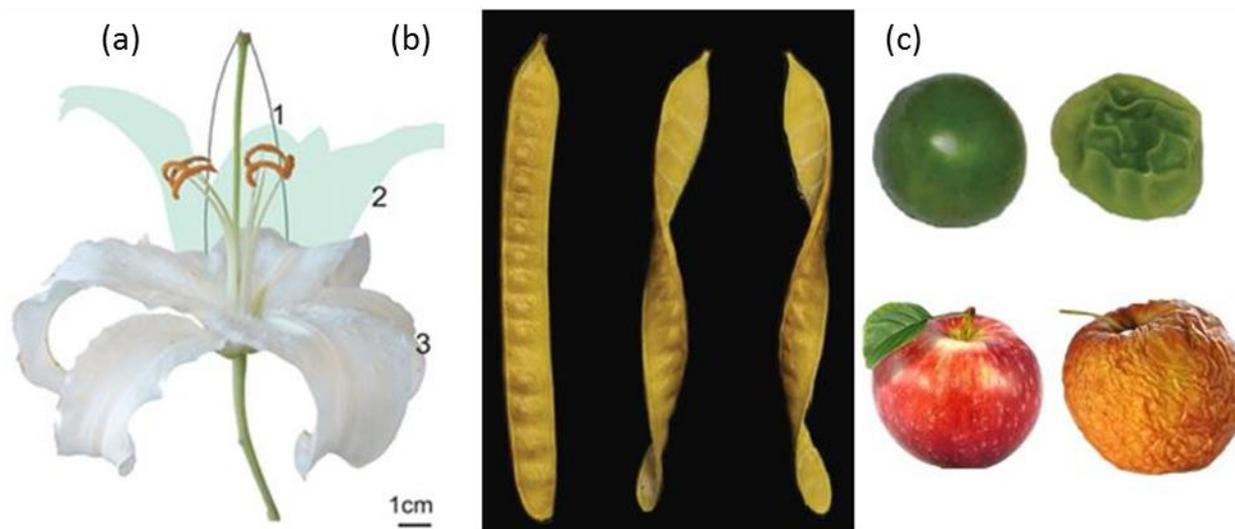
Figure 3.

Figure 3. Shape transformation in naturally occurring phenomena. (a) Representation of blooming sequence of lily flower. Dark line denotes the profile of the bud while the translucent light blue and white profiles indicate the partially-open and fully-open stages. (b) Stages of coiling of seed pods. Straight pods twist and coil upon dehydration and assume chiral profiles. (c) Surface pattern formation on green peas and apples, upon dehydration.

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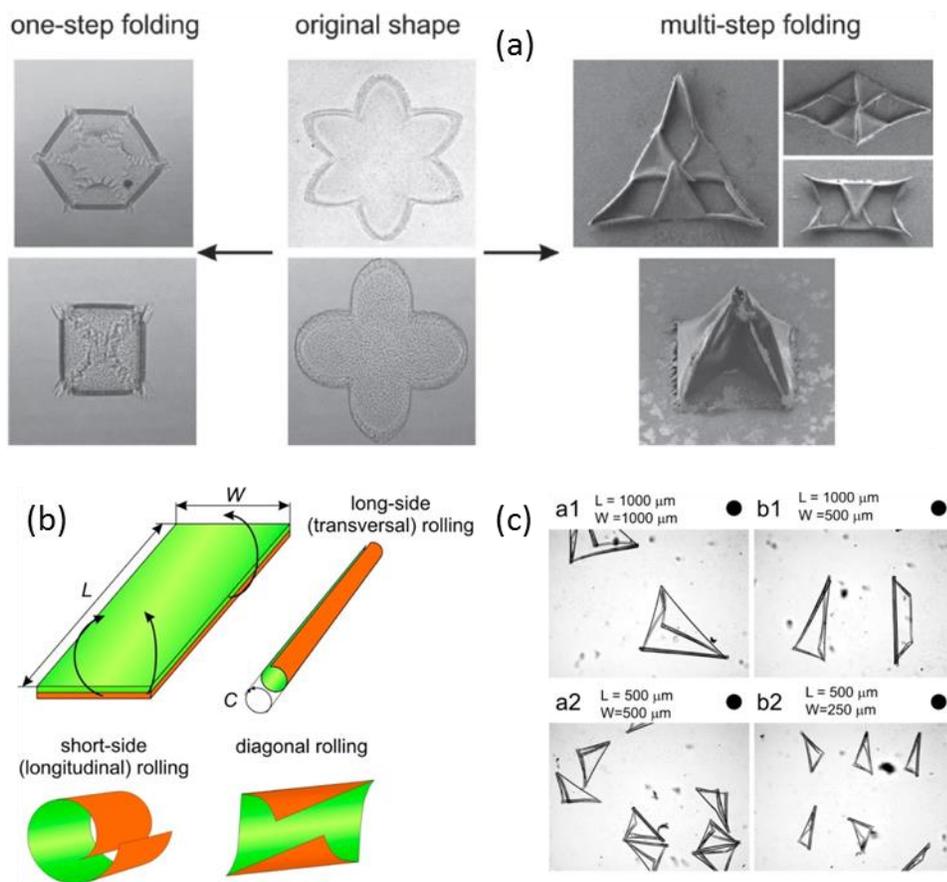
Figure 4.

Figure 4. (a) Illustrative images of bilayer structures undergoing linear and hierarchical folding to attain programmed structures. (b) Schematic of polymer bilayer strip folding into tubular structure, (c) Optical microscopy images of folded PNIPAm-PMMA bilayer of different length and width folding in longitudinal and diagonal pattern.

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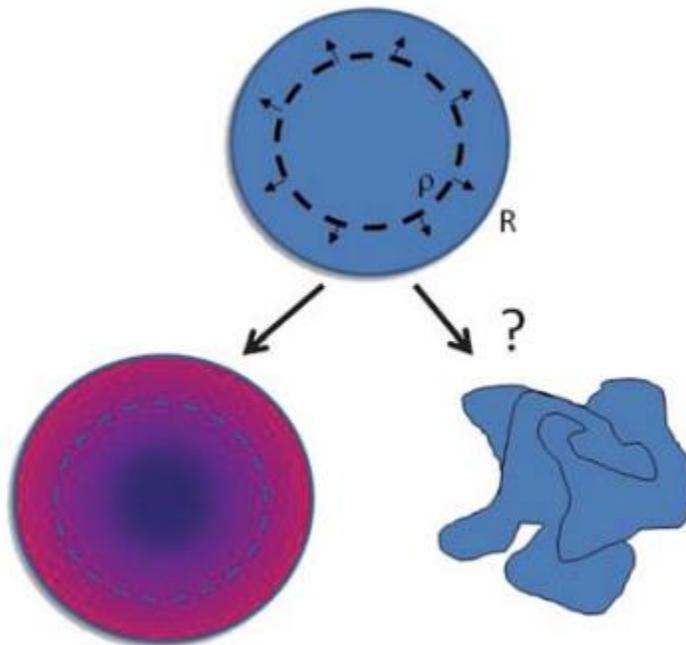
Figure 5.

Figure 5. (Top) Illustration of isometric swelling in a non-Euclidean plate. (Bottom left) The buildup of in-plane stresses (red color indicates tension, blue color indicates compression). (Bottom right) Possible 3D configuration as a result of pure bending and free of stress.

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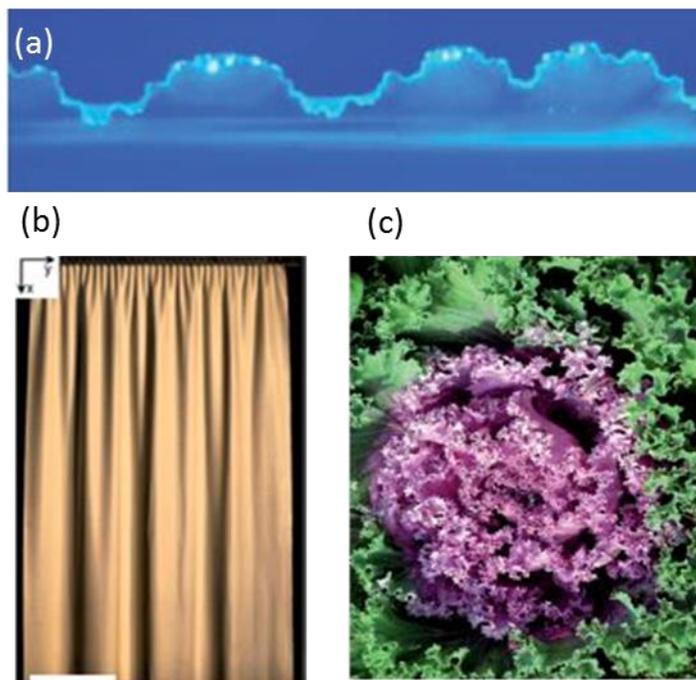
Figure 6.

Figure 6. Illustration of characteristics fractal-like wave pattern formation in natural systems. Hierarchical wrinkle formation on (a) the edges of torn plastic sheet, (b) suspended curtain and (c) cabbage leaves.

Reproduced from reference 51. (The Royal Society of Chemistry Journal).

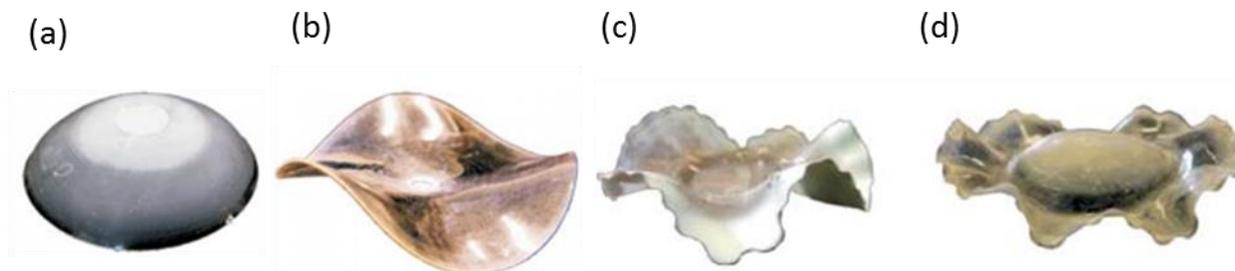
Figure 7.

Figure 7. Variety of possible structures that can ensue from the tuning of target metrics in a material. (a) a symmetric surface with positive Gaussian curvature, (b) thick sheet with hyperbolic metric exhibiting minimal curvature, (c) Thin sheet displays cascade of wavy pattern as a result of higher gradient in monomer concentration and (d) Existence of both positive and negative curvatures in a sheet.

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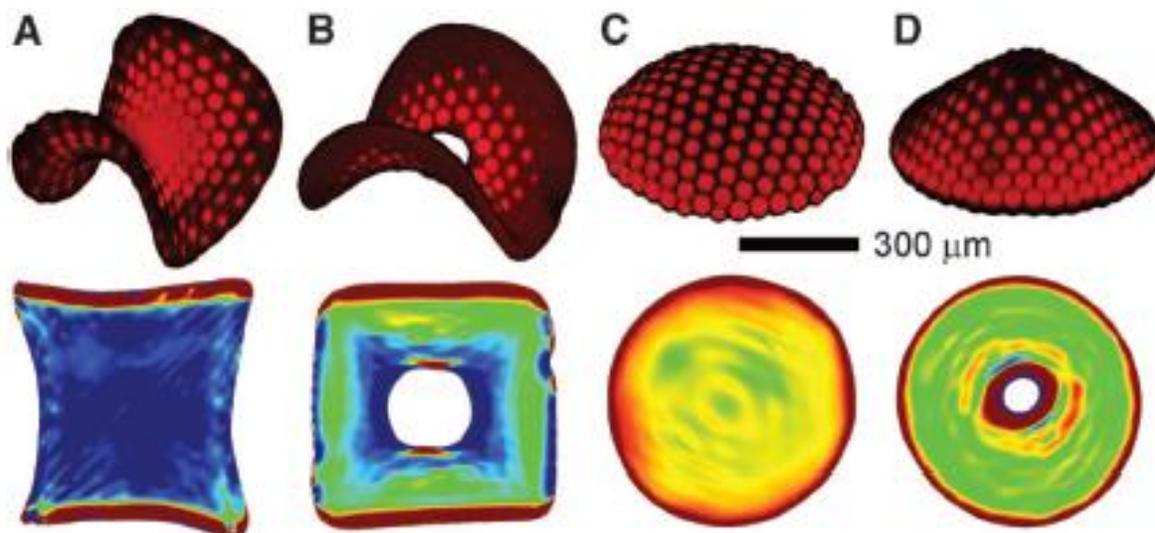
Figure 8.

Figure 8. (column wise) Series of 3D images of axisymmetric disks patterned by halftone lithography and the corresponding Gaussian curvature surface on the bottom (a) saddle like surface, (b) conical shape with an excess angle, (c) spherical cap shape and (d) a cone with a deficit angle.

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Figure 9.

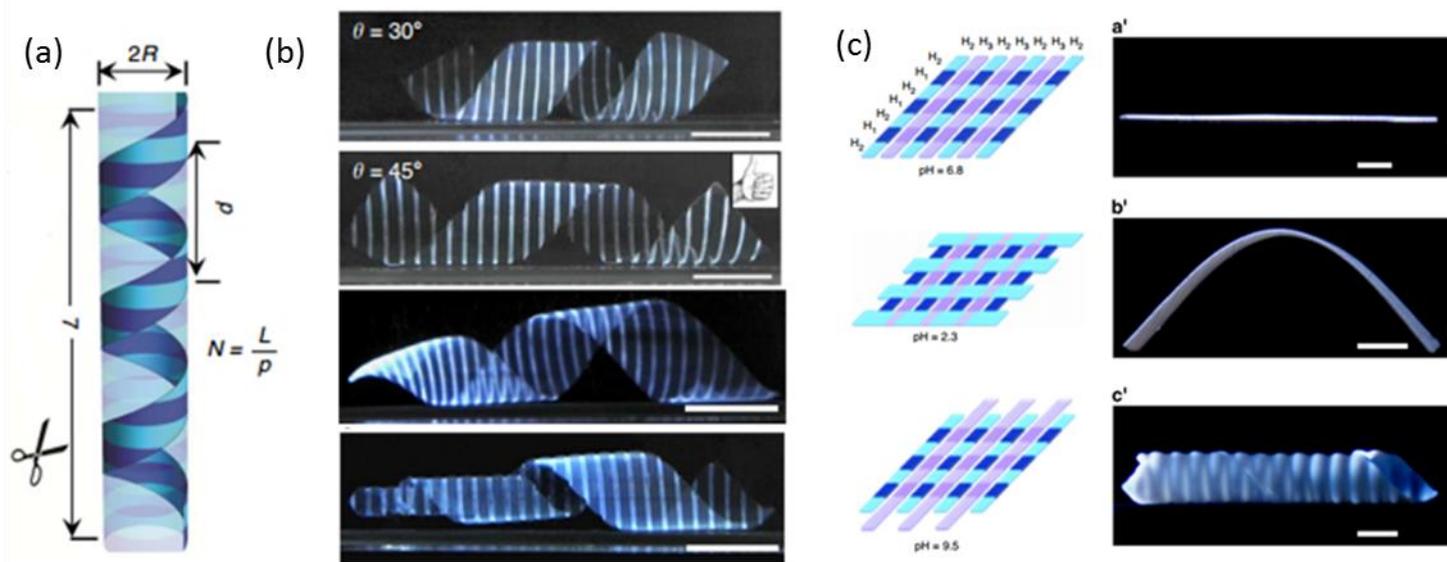


Figure 9. (a) Design criteria that dictates the characteristics of helices are radius R , length L , number of turns, N , and pitch p . (b) Top half illustrates the angle dependency of helix pitch and chirality of the helices. Bottom half demonstrates the effect of small-scale modulation to form conical helices. (c) Schematics and images of multiple shape transformations of the sheets in response to solvent pH. Scale bar for the inset (b) and (c) is 1 cm.

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Figure 10.

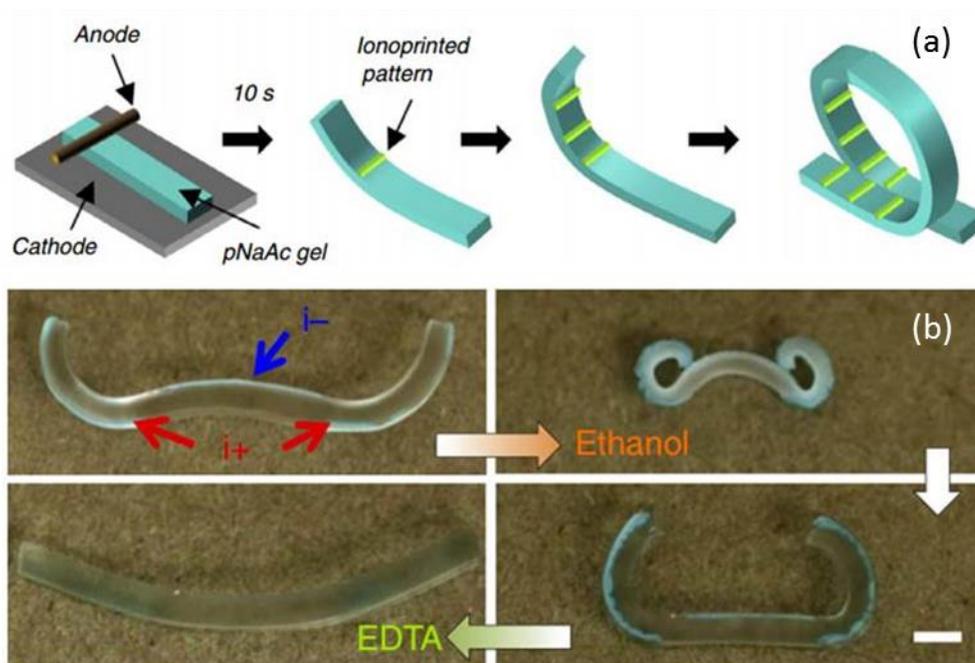


Figure 10. (a) Schematics of ionoprinting process; electroactive anode is employed to inject ions into the 3D hydrogel strip and the strip assumes a shape as a result of differential shrinkage caused by dehydration (b) Controlled and reversible shape transformation of the gels upon immersion in ethanol and EDTA. Scale bar, 5mm.

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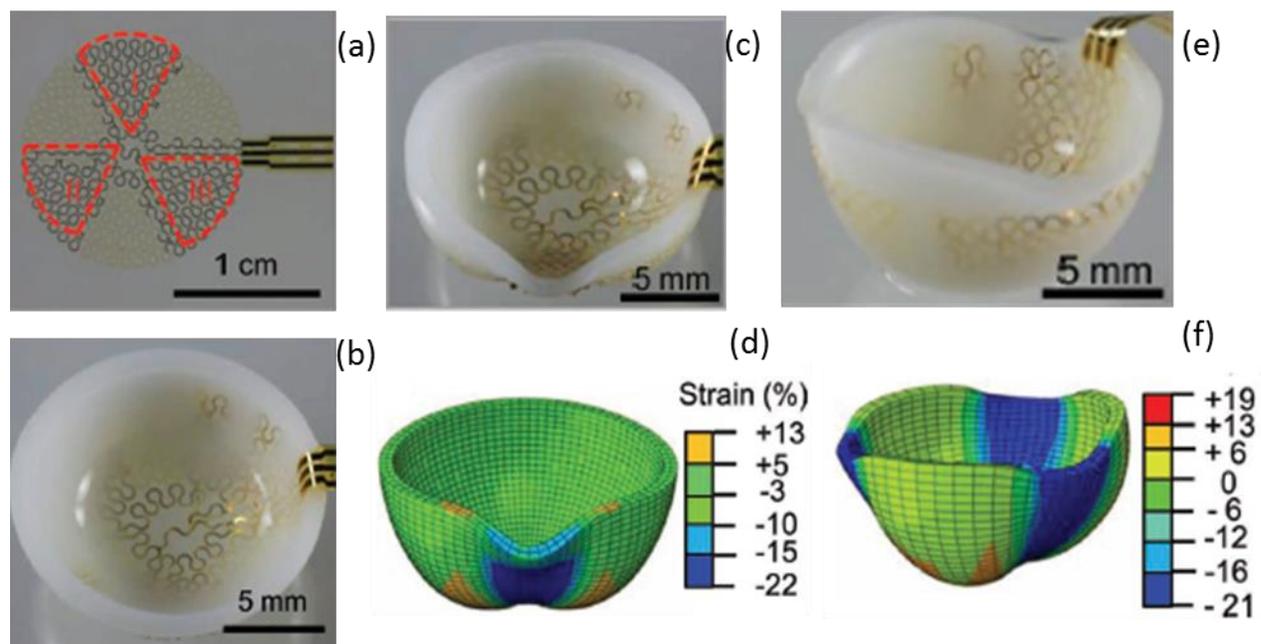
Figure 11.

Figure 11. (a) Optical image of ultra-thin mesh designed to have 3 distinct segments that can be controlled separately, (b) Hydrogel embedded with the mesh to form a hemispherical structure. (c) Optical image of hydrogel acquiring programmed shape upon activating one of the heating segments, (d) corresponding finite element method (FEM) simulation of the hydrogel mesh shown in image (c), image (e) shows the shape acquired by the hydrogel upon activating all of the heating segments and its corresponding FEM simulation in image (f).

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Figure 12.

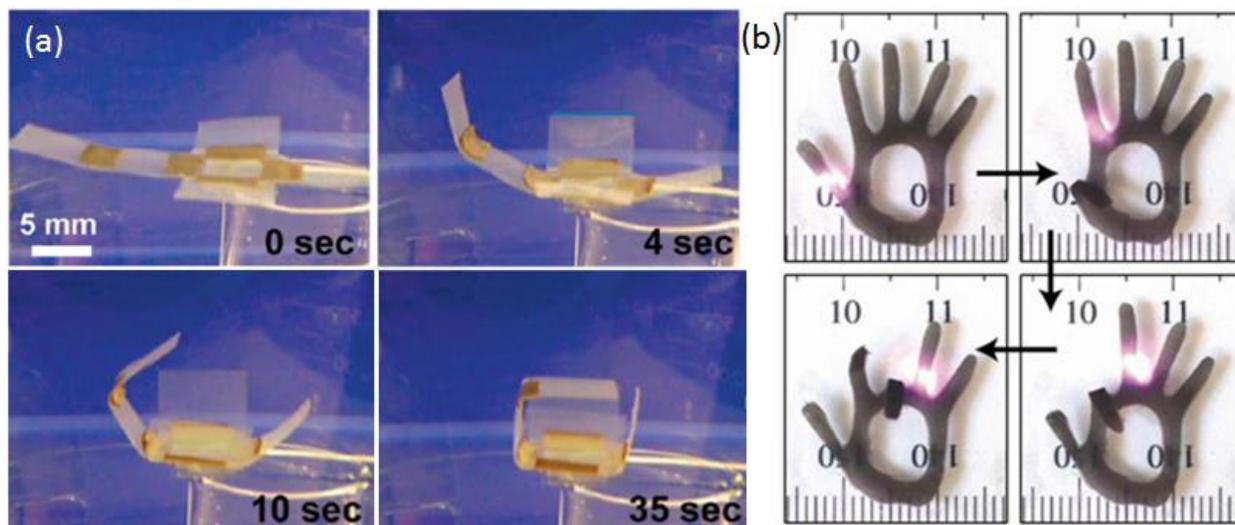


Figure 12. (a) Time-lapse optical images of PNIPAm/LDPE-SWNT composite structure acquiring preprogrammed cubicle shape in response to thermal actuation by immersion in hot water (left to right raster), (b) Series of optical images illustrating the NIR-photothermal actuation of hand shaped rGO-elastomer hydrogel. The wavelength of laser used in 808 nm.

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