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Engineering Materials ENGR 220

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4D Printing

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Abstract

Additive Manufacturing or 3D printing is in simple terms, the process of building a part by layering material according to a programmed path. There are many ways in which this is achieved. The variations include material of the part and how the binding of each layer occurs. The adding of material only where it is needed reduces the waste of milling parts by subtracting up to 80% of the raw material. This process has received the attention of industries trying to cut costs. The emerging 4D printing is an evolution of the 3D printing. It utilizes the properties of composite materials to transform flat 3D prints into complex shapes over time by adding an external stimulus. This reduces material waste, production time, labor cost, and has an increased strength, which makes it a viable manufacturing process.
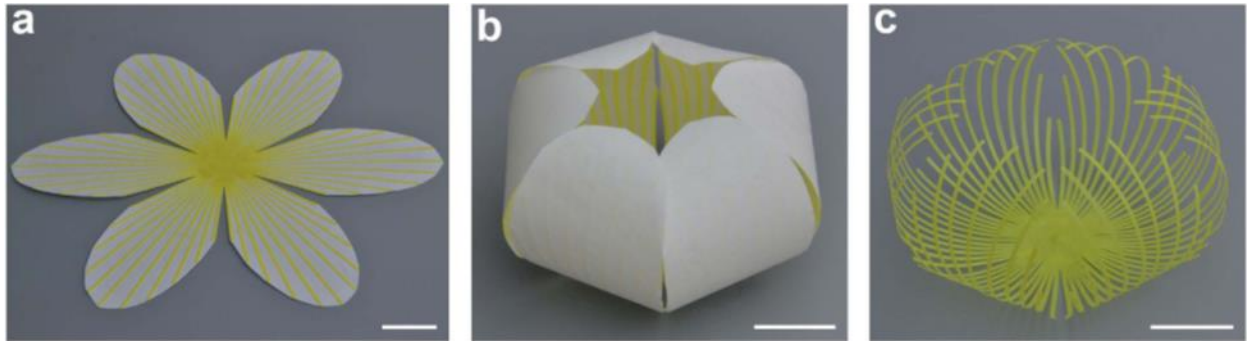

Figure 1. Example of 4D Print Transformation [1]

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Introduction

In 1980, Chuck Hall's idea for printing an object using the UV lights to cure layers of a photosensitive resin, was the spark of a 3D printing revolution. It took four years of painstaking work to give birth to the first stereolithography printer. The efforts produced a small cup and proof of concept in 1984. In 1986, he received a patient and started, 3D Systems Corporation. By 1990 three types of 3D printers were available and were the foundation for continued innovations.

The aviation and defense industries began using this technology in 1989, which lead to the funding of further improvements and innovations. Prototyping with the immediate 3D printing of parts and components cut months off research and development time and cost. This led to the development of additional printable materials and capabilities. This quickly turned into the production of custom parts in small quantities which avoided tooling production costs. Today, additive manufacturing is used in many industries and in many ways. Lower material cost, lower printers cost, and the tenfold increase in speeds, has now opened the door to the production of everything from sneakers, to concrete homes, and even space capable rockets.

Additive manufacturing specializes in the construction of complex designs, added functionality, the consolidation of parts, and lightweight materials with little or no waste. In an ever-increasing world of limited resources, we cannot afford to waste raw materials or time to keep production cost low.

3D technology now has the capability to print composite materials. In 2013, Skylar Tibbits introduced the concept of printing composite, smart materials for self-assembly[2]. This has ushered us into a greater capability for printed production, the 4D manufacturing model.
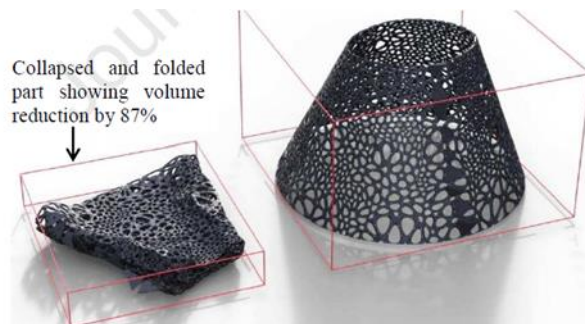
Figure 2. Printed Part Showing the Shape and Size Changing Features [3].

Motivation

This topic is an interest to me because of my Engineer Technology Degree and the rapid increase in the additive manufacturing field. I see continued growth in the field of additive manufacturing which required knowledgeable and skilled engineers. The 4D printing is an innovation of the 3D printing technology and just the beginning of a manufacturing revolution. I believe it shows potential for a rewarding career in both printer designs, print layout, and material property research.

Applications

1. Definition

a.   Additive Manufacturing (AM): also known as 3-dimensional (3D) printing, utilizes the two-dimensional layering of fused material to form a three dimensional solid shapes. 4D printing also falls under this title.

b.   4D: It is 3D printing of dynamic materials into flat shapes and then subjecting it to an activating stimulus which causes it to transform into complex shapes over a given period of time.

c.   Computer Aided Design and Dimensioning (CAD): Computer programs and algorithms with speed up the design and programming instructions for AM.

d.   Mathematic Modeling: Is the converted CAD model to a set of commands for the printer to carry out.

e.   Numerical analyses: the study of the 3D/4D data, which looks at the physical properties of materials and how they react. Solid data which can be used for engineering.

f.   3D Composite: refer to a polymer that has been reinforced with a solid particle (fibers, glass beads, etc.).

g.   Smart Materials: Smart materials have the special property which can vary their shape and properties once activated by an external supply of force. [4]

h.   Shape Memory: an effect or shape change effect is one of the dynamic methods designed for the deformation of materials.

1.1 The Class of 3D Materials

The 3D material consists of one material throughout the static part. Technology or printers with dual extruders can print with two materials but do not normally react with each other or change. Some of the most common are:

A.   PLA (polylactic acid)

B.   PETG's (glycol-modified polyethylene terephthalate)

C.   ABS (acrylonitrile butadiene styrene)

D.   ASA (acrylonitrile styrene acrylate)

E.   Nylon

F.   PC-ABS

1.2 The Main Types of 3D and 4D Printer platforms

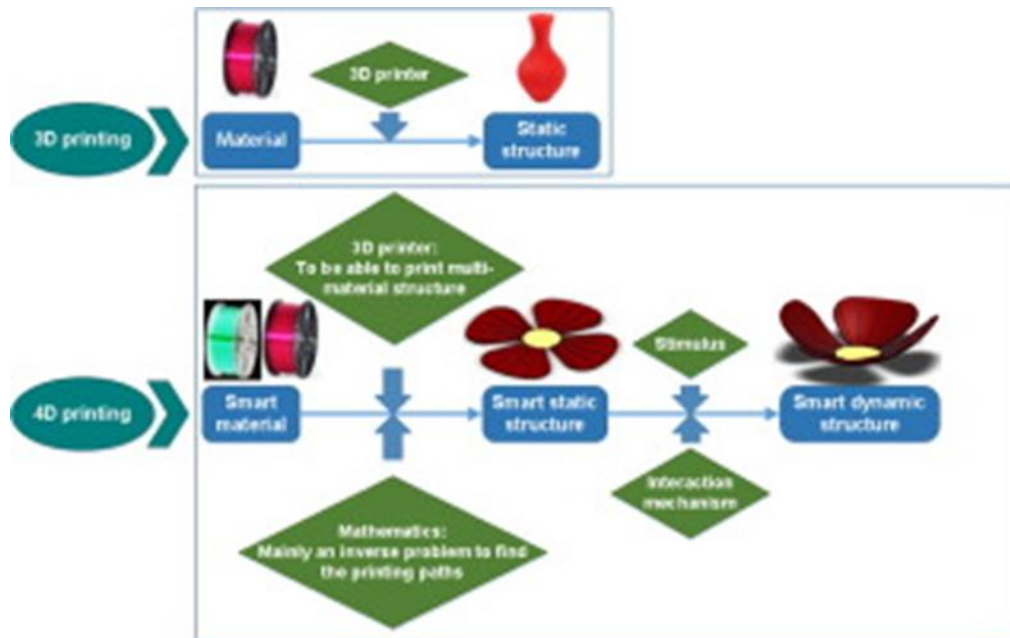Fig. 3: Schematic Representation of the Difference Between 3DP and 4DP [5].

1.2.1. Stereolithography (SLA) Printer

It uses focused ultraviolet light to cure a photosensitive polymer or resign liquid, one layer at a time as illustrated in Figure 4. The advantage of the SLA printer is its speed, machinability, and use in high-temperature applications.
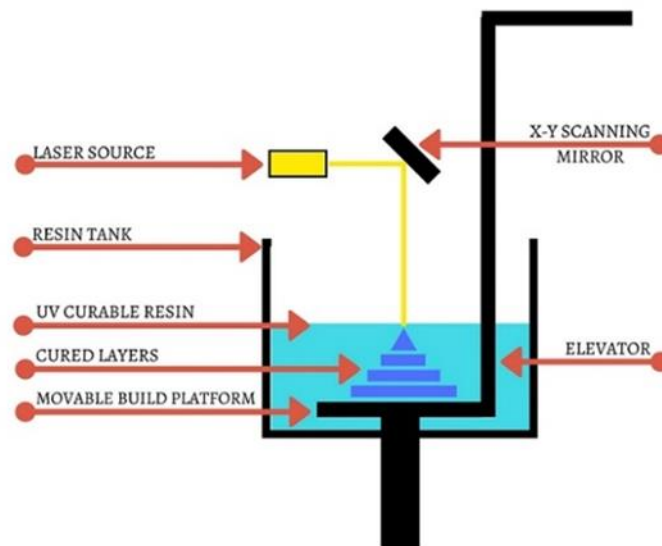

Figure 4. Components of Stereolithography Printer [6]

The liberty to alter the properties of materials, the resolution is the benefit of this method. Stereolithography method is applicable to produce electronic devices, jewelry, and fashion wear, and biomedical applications. The method is regularly creating a layer-by-layer structure using solidification of photo curable hydrogel liquid. UV–laser is utilized to scan the hydrogel, which leads to the creation of covalent bonds among the chains of the polymer and replicate of the above process, finally leading to the formation of layers. 4D printing process is feasible by managing the power of the UV–laser, speed of the scan, coverage time, wavelength, and spot size. [7]

1.2.2. Fused filament Fabrication/Molding Printers:

Most commonly use in 3D printing, Polylactic acid (PLA) and Acrylonitrile butadiene styrene (ABS) and are seen the most in homes. Figure 5 shows an example of printer. The PLA and ABS are thin filaments which are fed into a heated extruder and liquefied. The machine builds a single layer, one on top of the other. The layers melt together and cool into a solid plastic. These materials are cheap due to their use in injection molding. It also brings extensive options in color, and material properties. ABS is recyclable and PLA is biodegradable. Various other materials may be used, including polycarbonate (PC), PC/ABS hybrid, high-density polyethylene, polyphenylsulfone, and high impact polystyrene.
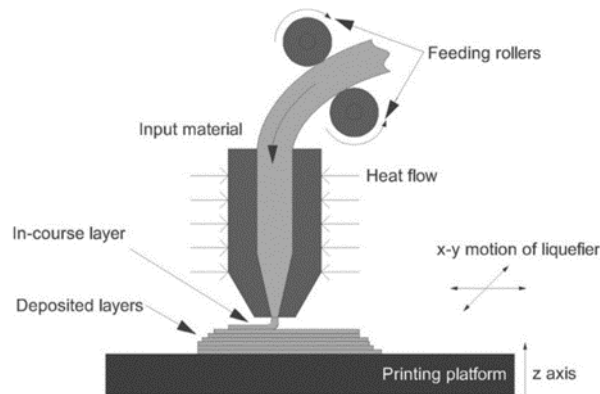
Figure 5. Schematic representation of a Fused Filament Fabrication [8]

The main concept of the fused deposition method is to permit shape memory or shifting heating mechanism. The deposition of the material undergoes thermo and mechanical training during the fusion deposition process. The influenced printing parameters are Speed, temperature, path of the deposition. Layer orientation and thickness are the design parameters to appreciate self-folding and self-twisting. Thermal expansion coefficient difference is accountable for the

shape shifting process. In the fabrication process, internal stress resides in the printed material as quick heating and cooling cycles happen. Improvement in 4D bio-printing is possible via printing of a bio-composite using fusion deposition process. The main intention is to improve the strength and stiffness with the actuation of self-shaping. The execution of the fused deposition method is more constructive in numerous engineering and biomedical applications[7].

1.2.3. The Powdered Bed Fusion:

This uses a powdered material and then a focused heat is applied through various methods to fuse the material to the previous layer. The heat may be applied by Selective Laser Sintering (SLS), Selective laser melting (SLM), or Electron beam melting (EBM), depending on the material being used and its thermal properties as illustrated in Figure 6. The benefit of this method is the powdered metals produce very good strength, hardness, durability, and reliability properties. A few powered metals worth noting are Ni-based superalloys, copper, aluminum, stainless steel, tool steel, cobalt chrome, titanium, and tungsten. This technology is being used heavily in the aerospace and medical industry. The disadvantage is the rough texture and needs post finishing, if desired. Also, the grain size of the raw material and direction of print can impact properties.
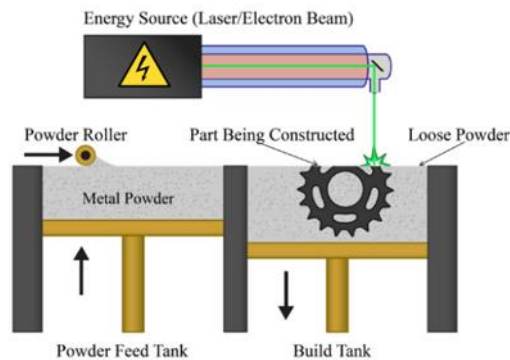
Figure 6. Powder Bed Fusion – Metal 3D Printer [9]

2.Properties Desired for 4D Printing

2.1 Thermal Responsive

Depending on the printing method, the temperature which materials melt and cool will have a large impact on the speed of the deposition of material, bonding of material, and energy cost. Thermal properties will also be the activation stimulus for some smart materials. For example, in 4D printing with hydrogel liquids, the time it takes solidify is temperature sensitive[2].

2.2 Photoresponsivity

A property of a material which absorbs light as heat. The color of the material and the light source determine the rate of the reaction[2].

2.3 Electoresponsive

Material property which responds to electric currents as an indirect stimulus. Blends if silicone elastomers and ethanol produces printed soft artificial muscles which contract by evaporating the ethanol through resistive heating. [10]

2.4 Magnetic Responsive

Other ways in which researchers have used stimulants to trigger the transformation of shape memory and smart materials is with the use of magnetic fields. In this case, the materials must be magnetic to be effective. This is usually achieved by doping the material with magnetic particles such as iron oxide. There are two main methods in which materials respond in the presence of magnetic fields. Firstly through the alignment of material under a magnetic field and the other is through magnetically-induced heating effects. An example of materials that respond to magnetic fields includes the work published by Huang on a supercapacitor made from a self-healing yarn consisting of Fe_3O_4, stainless steel yarns coated in carboxylate Polyurethane with PVA-H_3PO_4 gel used as a solid electrolyte. The strong magnetic forces from the electrodes resulted in beneficial reconnections of fibers to restore electrical conductivity. The self-healing capabilities, in this case, were possible through the abundance of hydrogen bond acceptors and donors in the supramolecular polymer. Although only the supramolecular polymer is self-healing, the magnetically assisted forces help to reconnect the yarns. Magnetically-induced heating was reported by Wei, they demonstrated a magnetically responsive ink for DIW made from iron oxide nanoparticles embedded within Polylactic Acid (PLA) polymer matrix. The magnetically responsive material began to uncoil when a 30 kHz magnetic field was induced the shape-changing properties. [11]

2.5 Moisture Responsive

Materials which respond to moisture are called hydrogels. Hydrogels are absorbed in an aqueous atmosphere to take up water still, it reaches the moisture saturation point. Hydrogels permit enlargement of 200% of their original volume and show good printability via ink writing and biocompatibility, which create hydrogels are unique moisture responsive materials. Mao,

printed a structure with the hydrogels since hydrogels are restricted in a single direction through stiff materials. As a result, an isotopically directed swelling is observed [3].
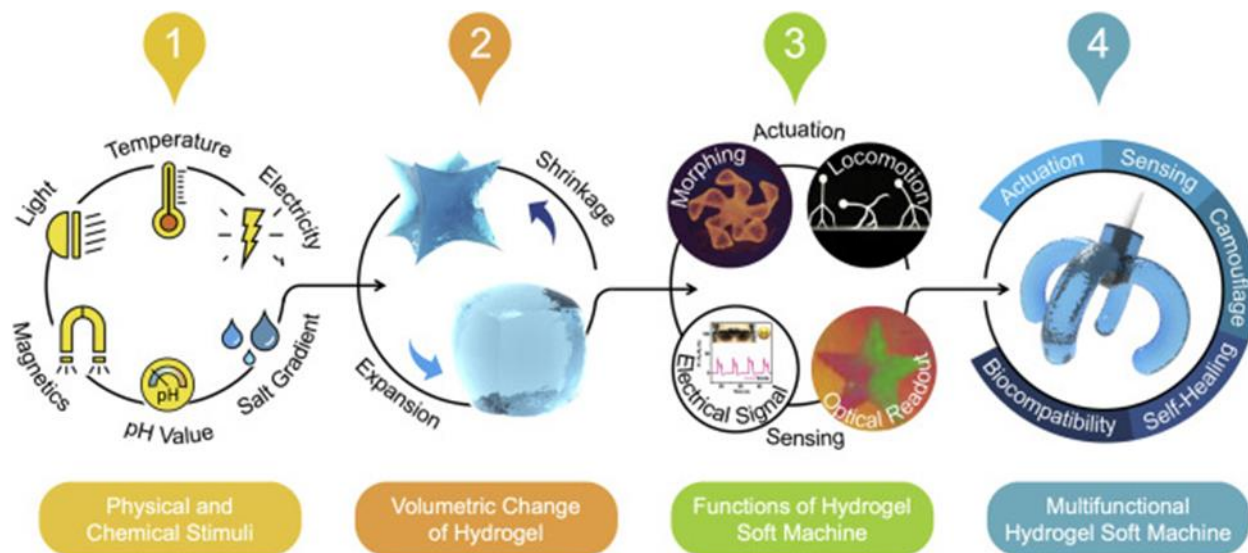

Figure 7. Illustration of Stimuli-Responsive Hydrogels [12]

3. Types of Stimuli

3.1 Electrical Voltage/Current

Electroresponsive hydrogels refer to a group of electroactive polymers (EAP) that swell or de-swell in response to the electrical signals applied (e.g. voltage, current). For example, when a voltage is applied across a layer of electroresponsive hydrogel, the electrical fields result in non-uniform ion distribution, which causes the osmotic pressure difference that results in the curvature changes of the hydrogel layer (Fig. 8). In general, the electroresponsiveness of hydrogels can be specifically designed using the EAPs with different ionizable functional groups. Several reported EAPs are poly (2-acrylamide-2-methylpropanesulfonic acid) (PAMPS), poly (acrylic acid) (PAAc), poly (4-hydroxybutyl acrylate) (poly (4-HBA)). The ionizable functional groups on the EAP backbones/side chains provide abundant fixed charges that enable fast ion localization in response to the electric fields, normally resulting in a short response time (0.1 s) and large mechanical deformations (~40% in strain) of EAP-based hydrogels. Besides selecting different EAP backbones, another approach is to add ionic compounds to enhance the electroresponsiveness of hydrogels. By adding the ionic compounds (such as lithium chloride (LiCl) and sodium chloride (NaCl)) in hydrogel matrix, the concentration of mobile ions increases, which thus induces faster hydrogel actuations in response to the electrical fields. The

fast and large volume change of electroresponsive hydrogel is similar to natural muscles, which can be utilized as biosensors and artificial muscles when employing an electrical stimulus[12].

3.2 Temperature

Thermoresponsive hydrogels are the most studied smart materials that can undergo dramatic and reversible volume changes as the surrounding temperature varies. The working temperatures of thermoresponsive hydrogels are based on the phase transition behaviors of thermosensitive polymers. For the thermoresponsive hydrogels with negative (inverse) thermosensitivity, the hydrogels exhibit aqueous insolubility at the surrounding temperature above their lower critical solution temperature (LCST), where aggregation of desolvated polymer chains occurs, defined as LCST behavior. For example, poly (N-isopropylacrylamide) (PNIPAAm) is a representative thermosensitive polymer that forms the hydrogel with negative responses. When the surrounding temperature is above its LCST (~32°C), the PNIPAAm polymer chains shrink due to the decreased water solubility (Fig. 8). On the other hand, polyacrylamide (PAAm) and polyacrylic acid (PAAc) are the typical polymer backbones of responsive hydrogels with positive thermosensitivity. As the surrounding temperature is above the upper critical solution temperature (UCST), the strength of waterepolymer interactions, in terms of hydrogen bonds or electrostatic bonds, become stronger than that of polymerepolymer interactions. The corresponding increase of hydrogel solubility is defined as UCST behavior. Moreover, by combining two types of thermosensitive polymers, for example the copolymers of sulfobetaine methacrylate (SBMA) and NIPAAm, the resulting hydrogels are managed to possess dual responsiveness to the varying temperatures above the UCST (15°C) and lower than the LCST (41°C). Of late, there is a growing interest in finetuning of the thermal responsiveness through molecular design, which provides new opportunities to develop various soft machine systems (actuators, robots, sensors, drug delivery systems) to fulfill different applications requirements.[12]

3.3 Light

Light is a particularly useful stimulus to remotely induce the volume changes of photoresponsive hydrogels upon light irradiation. Two main actuation mechanisms of photoresponsive hydrogels include reversible cross-linking reaction and photothermal excitation. Both of them can be realized by the incorporation of photoactive moieties within the hydrogel matrix. For the mechanism of reversible cross-linking, photoisomerization and photocleavage are

two prevalent approaches. Upon light irradiation, photo-initiative moieties, such as azobenzene (configuration changes) and spiropyrans (ring opening/closing reactions), can induce the photoisomerization within hydrogel matrices. On the other hand, photolabile protective groups (e.g. p-hydroxyphenacyl groups, o-nitrobenzyl groups, and triphenyl methane groups) are incorporated to achieve the photocleavage of hydrogels upon illumination. Sequential steps of light-induced cross-linking followed by de-crosslinking processes resulted in reversible contraction expansion of polymer chains. Several applications have benefited from the development of photoresponsive hydrogels, for example, self-healing hydrogels, soft actuators or robots with remote control, molecular machines and controlled drug release.

In addition to the photo-induced cross-linking reactions, light induced deformation can be achieved by the reversible dehydration & hydration processes. The reversible dehydration & hydration processes are induced by using selective illumination for localized heating. By incorporation of photothermal nanomaterials, the dehydration & hydration processes can be accelerated and intensified. The incorporated photothermal nanomaterials can rapidly convert light irradiation to heat dissipation, which induce the localized dehydration and thus the deformation of photoresponsive hydrogels (Fig. 8). Over the last two decades, many nanomaterials with efficient photothermal capabilities, including inorganic nanomaterials (e.g. gold (Au), neodymium oxide (Nd2O3), carbon-based materials, black phosphorus), and organic compounds (e.g. cyanines, porphyrins). have been incorporated into hydrogels to improve the photo responsiveness of resulting flexible composites. Compared with the reversible cross-linking mechanism, the actuation speed based on photothermal excitation is much faster (~10 times faster in angular speed), which is preferentially used in soft robots, and microfluidic devices[12].

3.4 Magnetic Field

Magnetic field is a favorable stimulus for specific applications because it can trigger remote actuation with a fast response time and still remain biocompatible even at high field strengths. The magnetic responsiveness of hydrogels is mainly achieved by the incorporation of external paramagnetic or ferromagnetic additives into polymeric matrix, which enables rapid and large actuating behaviors in response to magnetic fields. In such magnetically responsive hydrogels, the magnetic additives are classified into three main types: (1) metals and alloys (e.g. iron (Fe), iron & platinum nanoparticle (FePt), neodymium alloy (NdFeB)); (2) metal oxides (e.g. ferric

oxide (Fe2O3), ferrous ferric oxide (Fe3O4)); and (3) their functionalized derivatives. The first two types of magnetic additives can be incorporated in the hydrogel networks via physical entrapping. Subject to a non-uniform magnetic field, the magnetic additives engaged in the hydrogel matrix serve as the magnetic drivers that can experience a force proportional to the gradient of the applied field, which results in the motion of magnetic additives either forward or backward along the magnetic gradient. The motion of magnetic additives drives the deformation of the hydrogel structure via the entangled polymer chains. The third type of magnetic additives is generally prepared by the surface functionalization of magnetic nanoparticles, which can serve as both magnetic drivers and interparticle binders. Another mechanism of magnetically responsive actuation is through electromagnetic induction heating. By experiencing a rapidly alternating magnetic field (>10 kHz), heat can be generated by eddy currents in the thermoresponsive hydrogels incorporated with magnetic additives. One of the major features of induction heating is the rapid response time, rendering the applications of such magnetically responsive hydrogels in soft robots, biomedicines, and microfluidic systems [12].

3.5 pH Level

The pH regulation is particularly convenient for aqueous solution environments so that many studies of pH-responsive hydrogel focus on the applications related to the human body, such as drug delivery, gene delivery, and biochemical sensing. The actuating behaviors of pH-responsive hydrogels rely on the difference of osmotic pressure across the hydrogel networks upon exposure of pH variation. The pH-responsive hydrogels are usually fabricated by the polyelectrolytes that contain weak acidic or basic function groups. These ionizable groups can serve as the ionic barriers that only permit the ions with opposite charges to pass through. The directional ion localization leads to the osmotic pressure within the hydrogel matrix and induces the responsive deformation.

Based on the types of charges in the pendant groups of polymer networks, the pH-responsive hydrogels are classified into acidic or basic hydrogels. Common acidic hydrogels involve the polymer networks with pendant acidic groups such as carboxylic groups (e.g. PAAc and poly (methacrylic acid) (PMAAc)), sulfonic acid groups (e.g. PAMPS), phosphonic acid groups (e.g. poly (vinylphosphonic acid (PVPA)), or boronic acid groups (e.g. poly (vinylphenyl boronic acid) (PVPBA)). The basic hydrogels are usually composed of the polymers with pendant basic groups such as amine or amide groups (e.g. PAAm, poly (dimethylaminoethyl

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methacrylate) (PDMAEMA), poly (diallyldimethylammonium chloride) (PDADMAC)). The acidic or basic pendant groups undergo ionization with a dissociation constant (Ka for acidic pendant groups or Kb for basic pendant groups) which either accepts or releases protons in response to changes in environmental pH. For the acidic hydrogels, when the surrounding pH value is higher than the pKa, the acidic pendant groups become more negatively charged by releasing protons. As a result, there is an increase in the hydrophilic nature of the hydrogels and electrostatic repulsion between the polymer chains, leading to swelling of the hydrogel networks and vice versa (pH < pKa) (Fig. 8). In contrast, basic pendant groups in basic hydrogels become more positively charged by accepting protons at pH lower than the pKb value. This process results in the improved hydrophilicity of the polymer networks and increased electrostatic repulsion between the polymer chains, inducing the volumetric expansion of the hydrogel and vice versa (pH > pKb). Another classification is the amphoteric hydrogels that contains both acidic and basic monomers (e.g. PMAAc-co-PDMAEMA), which swell at pH < 3 and at pH > 5, and shrink at pH 3e5, reversibly. Many pH responsive hydrogels have been applied in various healthcare devices, such as soft microrobots and smart capsule switches[12].

3.6 Salt Concentration

Salt-responsive hydrogels swell and shrink when the salinity of tested solution varies, which is preferable for underwater applications. Many pH-responsive hydrogels are also salt-responsive, where the polyelectrolyte networks expand in pure water and shrink in salt solutions, attributed to the changes of osmotic pressure within hydrogel matrix. As the salt-responsive hydrogels are placed in low-salinity solutions, the dissociation of ionizable groups in aqueous solutions results in high charge density on the polymeric backbones and thus the intermolecular repulsion within hydrogel matrix; the volumetric expansion of hydrogel is observed. When the salt concentration increases, the charges of polymeric backbones are screened by the added counter ions, so the intermolecular repulsion force is attenuated, resulting in the collapsed polymeric network (Fig. 8). Particularly, a group of salt responsive hydrogel is composed of the zwitterionic polymers, for instance poly (carboxybetaine) and poly (SBMA). Zwitterionic polymers are a class of neutral polymers with both cationic and anionic groups on the same monomer unit. The hydrogel with zwitterionic groups exhibits strong anti-polyelectrolyte effect that exhibits lower solubility in pure water than in salt solutions. The reduced solubility in pure water is due to the strong electrostatic interactions between the zwitterionic chains (charge-

charge, charge-dipole, dipole-dipole interactions). In salt solutions, the increment of salt improves the solubility by screening inter- and intra-chain attraction between the oppositely charged groups, inducing the volumetric expansion. The salt responsiveness of zwitterionic polymers can be tuned by incorporating different types and concentrations of salts. Additionally, zwitterionic polymers demonstrate encouraging biocompatibility and antifouling capability, rendering various on/off switching applications in soft biomedical and bioengineering devices, such as biosensors and immunoassay systems. Some salt-responsive hydrogel actuators are composed of bilayer structures with a polyelectrolyte layer and a polyzwitterionic layer. The opposite responsive behaviors of polyelectrolytes and zwitterionic polymers in pure water and salt solutions can be utilized to regulate the bidirectional bending[12].
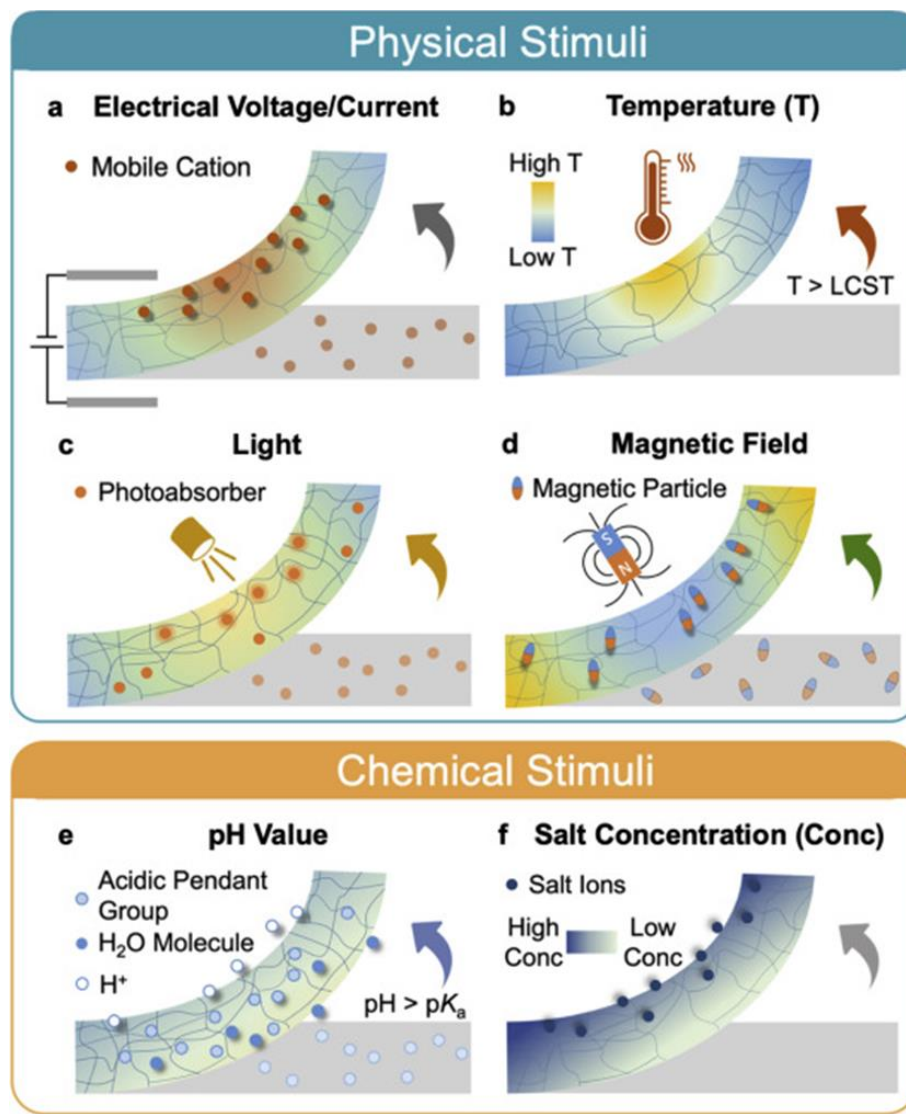

Figure 8. Working Mechanisms of Various Stimuli-Responsive Hydrogels [12].

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4 Shape-Shifting Behaviors

Shape-shifting behavior is one characteristic that distinguishes 4D from 3D printed materials and it is vital to understand it. These behaviors are studied from three primary aspects: mechanisms of shape shifting, types of shape shifting, and correlating stimulus. Many shapeshifting behaviors are a response to external stimuli such as temperature, light, pH, and water. Mechanisms of shape-shifting behaviors are constrained thermo-mechanics, constrained hydromechanics, unconstrained thermo-mechanics, unconstrained hydromechanics, unconstrained pH-mechanics, unconstrained thermo-photo-mechanics, osmosis-mechanics, and dissolution mechanics. Shapeshifting includes swelling, folding, bending, twisting, stretching/contraction, surface curling, surface topographical change, and the combined deformation of ending and twisting[12].

The shape-changing material (SCM) is a reversible material, i.e., it can change its shape when an appropriate stimuli is applied and return to its initial shape upon removal of stimuli. Shape memory materials (SMM) entail a programming step that can generally be divided into one-way SMM and two-way SMM. Moreover, three-way SMM has also been developed. It is worth noting that the SMM can hold its shape until a suitable stimulus is applied, whereas SCM cannot hold their interim shape when the stimulus is removed. A one-way shape-memory effect (SME) can be observed in situations where it is not possible to return a material to its original form after the shape-morphing effect has taken place. In contrast, a two ways shape memory can takes a temporary shape when the material transitions to its original form after the shape-morphing effect has materialized. The time taken by a material to transition can be influenced by internal and external factors. The internal influences relate to the properties of the material and cannot be modified; for example, the temperature at which the glass transitions, the density of the material, and its heat capacity. External influences are environmental conditions, for instance, temperature, rate of heating, and geometric thickness, which can be changed to manage the recovery time. It has been reported that the control of recovery time is directly impacted by the thickness of the object. Zhou explained how shape change effects (SCE) can differ, and that the magnitude of the observed change is directly correlated with the stimulus that is applied. At a high level, and depending on the environmental conditions, shape-memory materials possess both SME and SCE properties.

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Conventionally, the full process of the shape-memory effect of an SMM involves two fundamental operations: programming and recovery. The material is changed into its temporary configuration during the programming stage, after which it recovers its initial shape. However, this approach is inherently limited because it varies according to the properties of the material—for instance, its recovery ratio and strain—and the material may not fully return to its original state. Therefore, it is imperative that an appropriate material is selected to produce the object. In addition, a minor transformation hysteresis is needed to perform the repetitive action because it has a direct influence on power consumption and operational frequency. In some cases, a large transformation hysteresis is required to maintain the stable austenite phase within a broad temperature range as a means of preserving the shape. Transformation hysteresis is influenced by a variety of variables including lattice compatibility, the atomic radius of the alloying element, precipitation, and stress variation. Ge described the SME process by using the analogy of origami. A 3D object can be thermo mechanically programmed to perform a required function. For instance, 3D flat objects that incorporate appropriate hinges can be produced and, as a result of the use of suitable stimuli, be subsequently put together into the required shape. Later, through the application of appropriate stimuli, the end product can be recovered and returned to its initial form.

The change of shape, characteristics, and function of 4D-printed objects is the main role of stimulus. On the other hand, 4DP can also be performed on materials that can change color in reaction to electromagnetic waves like UV light and visible light. This is of immense value in the manufacture of effective camouflage or sensors. For instance, these materials can be placed within medical devices that are designed to monitor insulin or blood pressure levels. One example of the use of 4DP in this way can be observed in the work of Wang, who developed a 4D printing approach that was capable of simultaneously generating shape and color changes. The authors were able to control both shape and color morphing properties by adjusting the stimulus conditions and printing parameters. Ning employed an analytical modeling approach using a stationary coordinate to investigate the role of in-process temperature in metal powder bed additive production. Ali studied methods of optimizing shape in 3D printing composite polymers and subsequently proposed two new methods of shape optimization that harnessed novel technologies. Miao employed a self-assembly method where 3D objects modify their condition in response to external stimuli. For instance, origami represents the form of self-

assembly materials. The product is produced using multiple parameters so that it can change in a non-uniform fashion and, subsequently, maintain a given shape after the stimuli have been removed. Although temperature and water are frequently used as stimuli, other stimuli such as pressure, moisture, light, magnetic field, gravity, heat and light together, and the blend of water and heat, are gaining the attention of many researchers in recent years. However, the choice of proper stimuli strongly relies on the required application. This necessitates more research and development [13].

4.1 4D Printed Joints

The preferred joint for 4D printing includes two layers of material. The expanding material is placed above or below a layer of rigid material. The orientation of the rigid and expanding material dictates the folding direction. For example, if the expanding material is placed above the rigid material, the two surfaces will fold downward due to the downward force applied to the rigid material and vice versa. The rotational placement of the rigid and expanding material around the long axis of a one-dimensional line dictates the second folding angle in 3D space. If less expanding material is used, the folding force will be less but the folding time will be faster. If more expanding material is used, the force will be greater and the time for folding will increase. Rigid discs are printed at each vertex to control the angle of folding. The spacing between discs and the diameter of the discs dictate the precise angle (Figure 9). The discs rotate towards one another when the expanding material is activated, which causes them to physically hit one another and stop folding at the precise angle. If the discs are spaced further away from one another, the angle of folding will increase and vice versa. If the diameter of the discs increases, the angle of folding will decrease. However, in our models, the diameter of the discs was kept constant to lineup with the diameter of the linear members, thus the spacing between discs was utilized for custom angles.[14]

Figure 9. 4D Printed Joints Showing Custom Angles [14]

A series of tests, printed and repeated many times, were used to optimize the quantity and placement of materials to achieve precise and arbitrary angles (Figure 10). These empiric tests allowed for the calibration of digital model, simulation, fabrication tolerance and transformation dynamics. Further, the orientation of the part during the printing process created a unique grain direction and appeared to influence the final folded angle. Thus, data was gathered from each test and orientation from the printed structure to update a code that propagated custom angles into the digital model with adjusted tolerances for accurate real-world folding.[14]
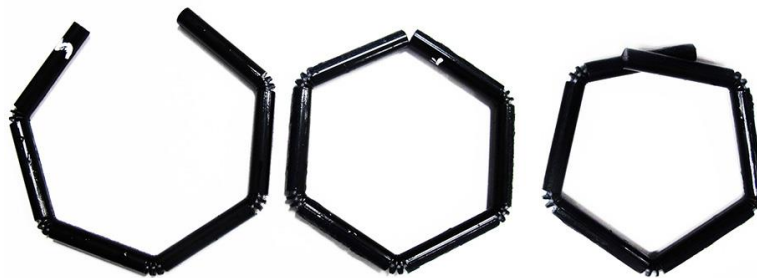
Figure 10. Calibration Tests and the Precision of Custom Angles after Self-Transformation [14]

4.2 Custom Angle Surfaces

To further demonstrate custom angle transformations, a series of flat structures were generated that utilize precise and arbitrary angles to fold from two-dimensional to three-dimensional objects. A truncated octahedron was created with hexagon faces and edge-joints (Figure 11). Similar to the protein strand, the spacing and placement of materials at each joint specified the desired fold angles. A code was generated to produce the custom angle joints and accommodate the data from calibration tests to ensure accuracy when folding.

After the file was generated and sent to the printer, the physical model was dipped in water and filmed to record the transformation process. Due to the manageable size of the model, hot water was utilized and the structure transformed within twenty minutes of activation. The calibration of the custom angles allowed for an extremely precise final structure where every edge aligned perfectly with neighboring edges. The truncated octahedron was removed from water and dried in-place to ensure the shape remains permanent. Given this technique, every known polyhedral that is able to be unfolded can now be 4D printed and self-transformed into a precise three-dimensional shape.

Two-dimensional printed structures emphasize the efficiencies of printing flat shapes, given its extremely quick print time and minimal material used. If the final truncated octahedron shape were printed, it would have taken far longer to print as compared to the flat surface even including the time for transformation, not to mention the amount of support material required. This technique points towards a future of shipping where flat-packed materials can be created, shipped flat then self-transform on-site for precise and volumetric products.[14]
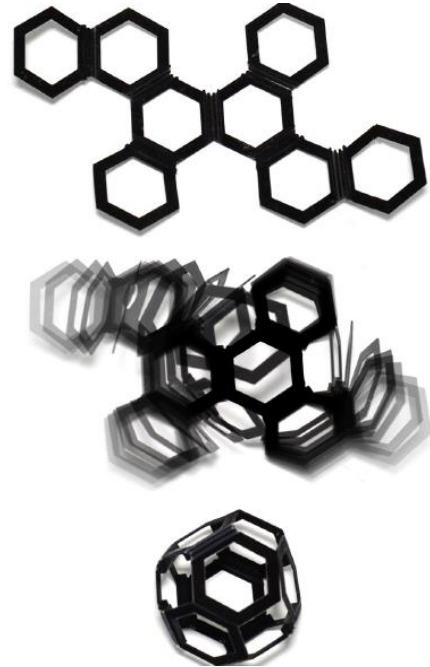
Figure 11. Transformation from a Flat 4D Printed Structure to a Precise Truncated Octahedron [14]

4.3 Curved-Creased Folding

A third prototypical structure was generated to challenge the possibilities of flat sheet transformations. This example attempted to transform a two-dimensional flat sheet into a three-dimensional doubly curved surface by utilizing a technique called, curved crease origami. Curved-crease origami is a process whereby curvilinear patterns with mountain and valley folds can approximate a doubly curved surface. Curve-crease structures offer a promising model for 4D printing since they can be printed flat to maximize efficiency while also precisely defining a transformation into complex surfaces with extremely rigid final structures. In this example,

concentric circles were generated with expanding material separated by rigid material (Figure 12). The rings oscillated between placing expanding material above or below the rigid surface, thereby creating mountain and valley folds. The volume in depth and width of expanding material were empirically tested to account for the force needed for transformation. Too much material ripped the surface apart and too little material did not provide enough force to go from the initial state to the final state. The final dimensions included 1/16" wide rings of expanding material with a depth of 1/64" emphasizing the extremely thin surface structure and great strength for folding. The printed curve-crease structure was placed in hot water and took roughly twice the amount of time to fold as compared to the truncated octahedron. The model remained static at the bottom of the tank for a long time before quickly popping into place. This strange behavior can likely be accounted to the forces accumulating in the surface until it reached a threshold that allowed the surface to jump into the mountain and valley positions. The surface then continued to fold until reaching the final, doubly curved state (Figure 12). The saddle-like structure remained extremely rigid and stable due to the conflicting forces of the curved surface. Due to this rigidity, unlike the previous models, the curved-crease surface did not unfold when taken out of water and dried.[14]
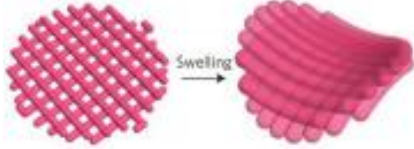

Figure 12. Transformation from a Flat 4D Printed Structure to a Curve-Crease Origami Structure Approximating a Hyperbolic Paraboloid [14]

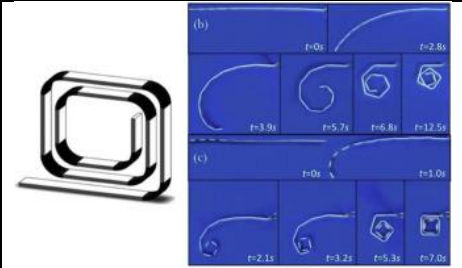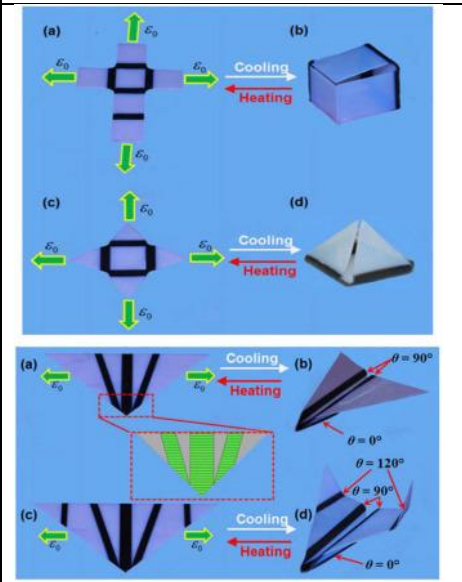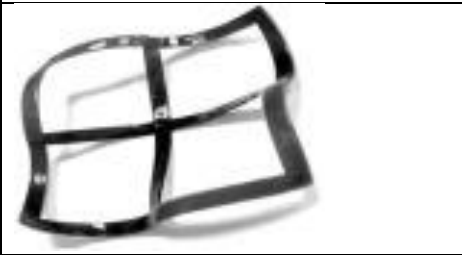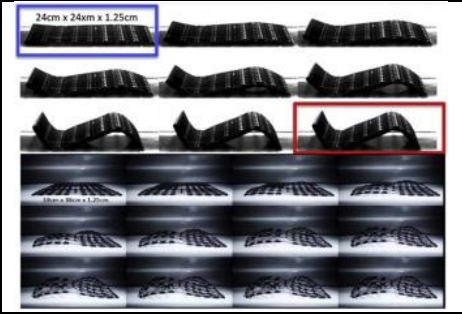**Summary**
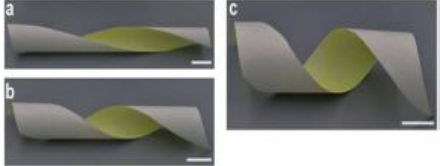
Smart material printing is being developed as an advanced manufacturing technology, which is 4D printing. The production of static structure in 3D printing was regarded as innovative technology, now by adding smart material and 3D printing, a new manufacturing paradigm is realized. 4D printing is emerging and has gained attention of many because of its structural response over time with stimuli. This paper provides a basic understanding of the fundamentals of 3D and 4D printing technologies, its concepts, and recent research successes as seen in Appendix 1. As Engineers it is our job to develop this technology and find greater applications for it.
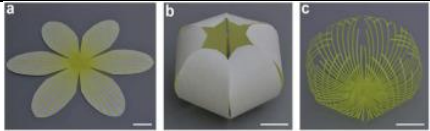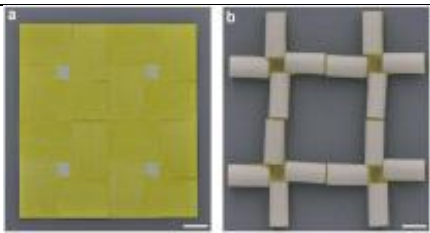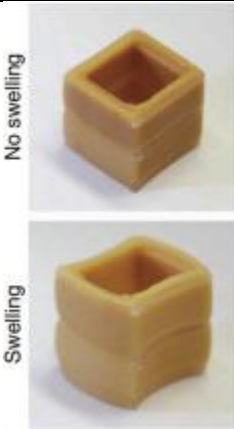
Appendix 1
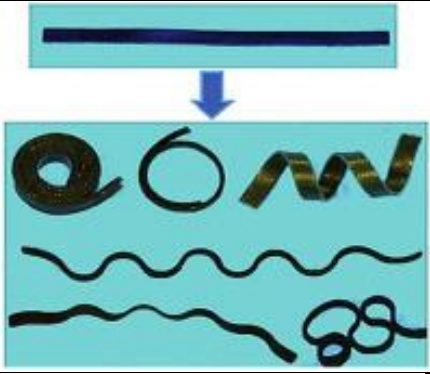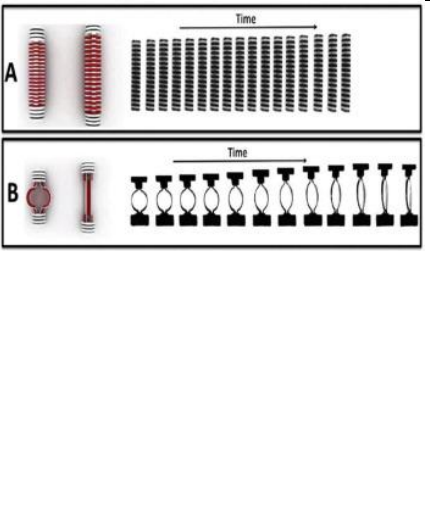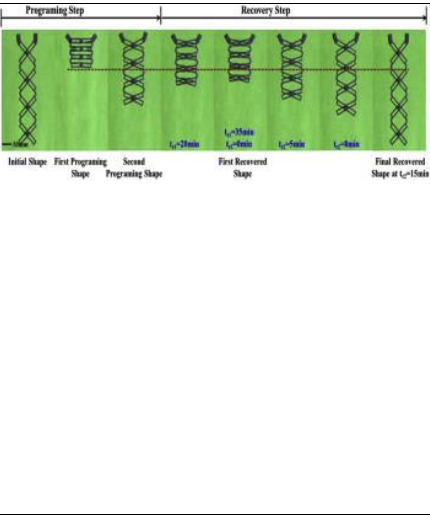
Table 1. Summary of Shape-Shifting Behaviors in 4D Printing [13].

Deformation Type	Illustration	Summary
Swelling		Hydrogel composite ink is formed from rigid cellulose threads embedded in a soft acrylamide substance. The hydrogel mixture swells when it is immersed in water. Utilizing water as a stimulus is an example of an unconstrained hydro-mechanism. The hydrogel's reaction to water results in the bending of its structure, providing an example of 2D-to-3D bending.
Folding 1D-to-2D		The composition of a single strand is made up of connected bars consisting of active materials and rigid disks. At a location between the bar's joint, two of the disks are printed as a limiter. Because this test utilizes water as the stimulus for the transformation, it can be considered an example of an unconstrained hydro-mechanism. Various shape-shifting designs in this structure can be achieved through manipulation of the rigid materials' position and volume.
Folding 1D-to-3D		A single 46-cm long strand was printed using two separate materials. One material was porous to allow for water absorption and the other was a rigid composition that was less porous and absorbent. This single strand transformed into a hard, wire-framed 3D cube after it was submerged in water. However, the rigid elements were unaltered by the process.
Folding 1D-to-3D		This study utilized water and temperature as the stimuli. After the structure was submerged in a 200-gallon tank of water, the researchers studied how the action affected the crambin protein.
Folding 2D-to-3D		This experiment illustrated unconstrained hydro-mechanics by first beginning with a 2D flat plane object, which utilized a combination of rigid and active materials. After being submerged in water, the plane's surface transforms (i.e., folds) into a sealed-exterior cube with filleted edges.

Folding 2D-to-3D		A 2D strip was transformed into a 3D shape using a series of self-folding steps. They utilized heat in the standard shape memory cycles, in conjunction with the routine recovery and programming steps, to prompt the shape-shifting transformations.
Folding 2D-to-3D		Origami boxes, pyramids, and airplanes were formed using self-folding transformations from the original 2D flat sheets to 3D geometries. They utilized heat in the standard memory cycles, in conjunction with the routine recovery and programming steps, to produce these shape-shifting transformations.
Surface Curling 2D-to-3D		A 2D surface grid that was created through layers of alternating elements. By applying the unconstrained hydro-mechanism, the submerged structure is capable of transforming into a mathematical sinusoidal shell.
Surface Curling 2D-to-3D		The 2D-to-3D shape-shifting behavior of a structure presenting with varying curling characteristics is demonstrated. The structure is composed of rigid and active materials and the shape-shifting behavior is allowed by a stress mismatch between these two materials from their altered swelling properties while they are in the water.

Twisting 2D-to-3D		Twisting of a 2D sheet of material into 3D shapes for helical formations using various spiral degree configurations is shown. Since the stimulus used in this experiment was heat, it is an illustration of the unconstrained thermo-mechanism. the fibers were printed at certain angles, it could stimulate a twisting behavior. Subsequently, if the print angles of the active fibers were altered, the final twist angle would also be altered.
Surface Topographical change 2D-to-3D		The transformation of a 2D flat sheet into a curved-crease 3D origami structure is shown. The flat sheet used in this test was made up of a sequence of parallel circles composed of expanding material. These concentric circles were divided by a rigid element. The observed shape-changing behavior was facilitated by the difference in stress between the active and rigid elements from their swelling characteristics while submerged.
Surface Topographical change 2D-to-3D		Within a 0-min, 30-min, and 24-h time period of coming in contact with the stimulus, three different shapes developed. The various swelling ratios between the rigid and active elements determined these resulting sinusoidal structures. The concentrations of the utilized elements varied when measured from the center of the disc to its perimeter.
Bending 1D-to-2D		An example of 1D-to-2D shapeshifting, which involves a linear strip formation that consists of alternating segments of active and rigid materials. When submerged in water, this formation is capable of transforming into a specific sinusoidal structure. This type of shapeshifting is an example of the unconstrained hydro-mechanism through the utilization of self-bending deformations.
Bending 2D-to-2D		The self-bending transformation experienced in 2D-to-2D bending is established based on the osmosis mechanism. In a 4D bio-printed network of droplets, the self-bending characteristics of the elements convert the rectangular network into a circle.

Bending 2D-to-3D		The multi-shape memory effect brought about by the self-bending characteristics produced during the conversion of a structure from 2D to 3D is shown with regard to a smart trestle. Heat is used as a stimulus in this experiment, and the shape-shifting characteristics were created in the common shape memory cycles in conjunction with familiar recovery and programming steps.
Bending 2D-to-3D		The multi-shape memory effect brought about by the self-bending characteristics produced during the conversion of a structure from 2D to 3D is shown with regard to an active helix shape. Heat is used as a stimulus in this experiment, and the shape-shifting characteristics were created in the common shape memory cycles in conjunction with familiar recovery and programming steps.
Bending 2D-to-3D		The multi-shape memory effect brought about by the self-bending characteristics produced during the conversion of a structure from 2D to 3D is shown with regard to an active wave shape. Heat is used as a stimulus in this experiment, and the shape-shifting characteristics were created in the common shape memory cycles in conjunction with familiar recovery and programming steps.
Bending 2D-to-3D		The multi-shape memory effect brought about by the self-bending characteristics produced during the conversion of a structure from 2D to 3D is shown with regard to a smart insect-like structure. Heat is used as a stimulus in this experiment, and the shape-shifting characteristics were created in the common shape memory cycles in conjunction with familiar recovery and programming steps.
Bending 2D-to-3D		The multi-shape memory effect brought about by the self-bending characteristics produced during the conversion of a structure from 2D to 3D is shown with regard to a smart hook. Heat is used as a stimulus in this experiment, and the shape-shifting characteristics were created in the common shape memory cycles in conjunction with familiar recovery and programming steps.

Bending 2D-to-3D		In this experiment, an intricate, flower-like structure was formed using 2D-to-3D self-bending behaviors stimulated by heat. This "flower" was created by tearing off a portion of the 3D structure. In this instance, the shape-transforming characteristic is produced by the various thermal expansion coefficients of the selected active and non-active materials.
Bending 2D-to-3D		An additional experiment that was performed that is similar to the previously described flower-like experiment. In this specific experiment, a 3D periodic formation was created from a 2D sheet comprised of four periodic cells arranged in a square. Inside each cell were one primary area and four neighboring rectangles.
Bending 3D-to-3D		An example of a 3D-to-3D self-bending as experienced in a bio-printed formation is shown. This shapeshifting transformation is prompted by the dissolution of a suitable material in an equally suitable solvent.
Bending and Twisting 2D-to-3D		The 2D-to-3D bending and twisting transformations shown are examples of an unconstrained hydro-mechanism. In this type of shapeshifting transformation, the structures are formed through the combination of the bending and twisting behaviors with intricate, flower-like morphologies. After being immersed in water, the structure can transform its shape into that of a flower.

Bending and Twisting 2D-to-3D		Another example of 2D-to-3D transformation produced by a combination of bending and twisting is shown by a structure composed of shape-memory materials. In this instance, heat prompts the initial object to transform into an arbitrary shape.
Stretching/ Contraction 1D-to-1D		(A): in 1D-to-1D transformations (i.e., expansion and contraction), water is utilized as the stimulus. The 4D printed formation is comprised of alternating tiers of hard discs and active hydrogels. Once the formation is submerged in water, the hydrogel components begin to swell as the discs remain unchanged. Pre-determined linear shape-shifting behavior can be experienced by modifying the ratio of the expandable hydrogels to discs. (B): a ring is stretched into a bar. The adjustment of the stretching length is by controlling the radius of the ring and immersing the structure in water over time.
Stretching/ Contraction 1D-to-1D		Heat is applied as the stimulus and the shape memory cycle is the basis of its linear shape-shifting abilities. The shape memory cycle consists of the typical programming and recovery steps. Temperature negatively affects the length of the subject formation. Throughout the last step of the recovery cycle, the formation reverts back to the original programming step in which the temperature once again increases from 50 °C to 80 °C. This cycling procedure illustrates that the formation was capable of completely recovering its original shape contingent upon the constant decrease in temperature.

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