A Review on Printing of Responsive Smart and 4D Structures Using 2D Materials

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1. Introduction

3D printing (a.k.a. additive manufacturing) is a bottom-up approach that translates the software model of a structure into a printed object by layering printed materials (“bit to it”).[1] It is revolutionizing the manufacturing industry due to its simple implementation, low cost, waste reduction during fabrication, outstanding customization, and fast prototyping.[2] It is a material-efficient technique that could decrease the CO₂ emissions between 130.5 and 525.5 Mt by 2025 due to the low amount of energy employed during manufacturing, the delocalization of the production processes, and the lightweight of the printed parts.[3] It can also democratize the production procedures for large companies and the public by decentralizing the fabrication of components, tools, and replacements. 3D printing comprises a range of techniques that utilize different materials such as plastics, metals, and ceramics in diverse forms, from filaments/pellets to powders and liquid solutions/pastes.[4] The 3D printing techniques are categorized according to the “ISO/ASTM52921” standard and are[5]:

1) Binder jetting that utilizes a liquid bonding agent selectively deposited to bind powders of materials.
2) Directed energy deposition in which concentrated thermal energy melts materials and fuses them as they are being deposited.
3) Extrusion in which material is dispensed through a nozzle to create the desired structure. Fused deposition modeling (FDM) and direct ink writing (DIW), which extrude/print layers of thermoplastic polymers and/or ceramics paste, are classified in this category.
4) Material jetting that deposits selectively droplets of material to obtain 3D structures.
5) Powder bed fusion that utilizes thermal energy to fuse a powder bed region selectively. Selective laser sintering (SLS) that sinters powders of materials (e.g., metals) through high-power lasers is the predominant 3D printing process of this kind.
6) Sheet lamination in which laminates of materials are joined to construct a component.
7) Vat photopolymerization that uses liquid photopolymer in a vessel to controllably cure them by light-activated polymerization. Stereolithography (SLA), which exploits light to cross-link liquid monomers into polymers, is the most utilized 3D printing technique of such type.

Considering the variety of printing approaches and the ever-growing palette of printable materials, the global market for

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3D printed products is forecast to grow 17% per year until 2024 and exceed $24 billion, with more than 120,000 patents filed in 2019.[6–7] Furthermore, 3D printing is a thriving research field (Figure 1a) that has delivered breakthroughs in areas as diverse as bone engineering,[8] food fabrication,[9] thermoelectric generators,[10] fashion,[11] bionic organs,[12] robotics,[13] composite science,[14–16] waste valorization,[17] flexible electronics,[18] and tactile sensors.[19]

The 3D printing of composites containing nanomaterials can link the advantages of printing with the broad spectra of features of nanoparticles and their diverse characteristics.[20–24] In particular, 2D materials offer a unique combination of morphological, optoelectronic, electrical, thermal, and mechanical properties peculiar to this class of materials in light of the myriad of production methods, chemistry, and structural features.[25–27] As such, 2D nanomaterials can be formulated in high-performance powders/dispersions/pastes that are ideal for direct implementation in most 3D printing processes.[28–31] Graphene-related materials (GRM) are the most investigated 2D materials due to their multifunctional properties, industrial-scale availability, and easiness of compounding with polymers, metals, or ceramics.[32–35] They have advantages compared to, for example, spherical nanofillers such as carbon black (CB) since the morphological characteristics, mechanical strength, and electrical and thermal conductivities enable multifunctional composites at lower filler loadings.[36] Indeed, 3D printing of GRM composites and inks has already been applied to thermal management,[37] supercapacitors,[38–39] batteries,[39] conductors,[40–44] composites,[43,45–48] aerogels,[49] and scaffolds,[50] amongst others, and is a field with hundreds of paper published in the last few years (Figure 1a) and already thoroughly reviewed.[41,50–53] Recently, other composites and inks containing 2D nanomaterials such as MXenes and hexagonal boron nitride were 3D printed for energy storage[54–56] and thermal management[57–58] applications, respectively.

To date, 3D printing has predominantly focussed on making structural devices, particularly compared to 2D printing (e.g., inkjet, screen, and gravure printing), where a range of functional devices has been produced.[59] However, there are two exciting areas of research in 3D printing where functionality is being incorporated (Figure 1b):

1) 3D printing of deformable and stimuli-responsive devices
2) “4D printing” of devices with a “programmed” change in properties/morphology over time.

The 3D printing of deformable and stimuli-responsive (a.k.a. smart) materials enables applications and new devices in construction, smart sensors, and aerospace, among others.[60–62] The most common external stimuli used to trigger and control the modification of physical/chemical properties of smart materials are the changes in electrical, magnetic, thermal, mechanical, moisture, and pH.[63–97] The 3D printing of smart structures is achieved by assembling intrinsically stimuli-responsive materials[98–100] assembling multimaterials,[98,101] or realizing composites[101–102] with nanomaterials.[101–105] This last approach was exploited, for example, to improve the piezoelectricity of 3D printed stimuli-responsive material by printing diverse polymers such as polyethylene glycol diacrylate or polyvinylidene fluoride with piezoelectric barium titanate nanoparticles.[106–107] Stimuli-responsive structures containing diverse nanoparticles have also been printed in the field of strain sensing[108–112] and self-healing.[113–114]

Skylar Tibbits first proposed 4D printing in 2013.[115] 4D printed structures are 3D printed devices that modify their shapes, properties, or functionalities in a programmed way (i.e., dependent on time) after an external stimulus is applied (Figure 1b).[116–117] Although at a young age, 4D printing is proliferating, as shown in Figure 1a, and has enabled structures unachievable with standard 3D printing, including the mimicking of dynamic living tissues[5,118] and plant structure/nastic movement,[118–119] autonomous robots,[120] self-constructive structure,[121] printed active origami,[122] and adaptive wind turbine blades.[123] The principal stimuli used to achieve the shape/property changes over time are water/solvent immersion, heat
and pH change, voltage/current or magnetic field application, or these combined approaches.[324–325]

Initially, 4D printing exploited shape-changing polymers, or an assembly of materials with a different deformation to a stimulus (e.g., swelling in a liquid or shape change due to heat/light) arranged to transform and alter form over time after the appropriate stimulus.[98,113] However, as with standard 3D printing, nanoparticles can give significant benefits for the trigger and/or the stimuli responsiveness in terms of reaction to multiple stimuli and speed of the response, respectively.[98,126–127]

For example, silica nanoparticles were blended with a shape memory photocurable polymer to reduce the resin curing time and improve the mechanical properties and shape memory mechanism.[128] Silica nanoparticles were also mixed with micro-cellulose and waterborne polyurethane to improve the printability and strength of these matrices while maintaining their thermal-driven shape memory.[129] A plant-minicking shape morphing system driven by hydration was printed by direct ink writing onto a composite constituted of acrylamide and oriented nanofibrillated cellulose that swelled anisotropically.[128] Recently, a nanocomposite of CB and polylactic acid matrices or gels offer the opportunity to modify their functionalities compared, for example, to 1D ones. Indeed, they comprise a family of nanomaterials that spans a wide range of properties due to the specific features of each 2D nanoflakes type. GRMs exhibit high thermal conductivity, excellent electron mobility at ambient temperature, high aspect ratio, significant modulus of elasticity, and high electrical conductivity.[133–135]

2D nanomaterials coupled with other materials such as polymers or gels offer the opportunity to modify their functionalities to become “smart” and/or enable 4D printing. 2D materials are highly suited for 3D printing dynamic and functional structures compared, for example, to 1D ones. Indeed, they comprise a family of nanomaterials that spans a wide range of properties due to their thermal-driven shape memory.[128] A plant-minicking shape morphing system driven by hydration was printed by direct ink writing onto a composite constituted of acrylamide and oriented nanofibrillated cellulose that swelled anisotropically.[128] Recently, a nanocomposite of CB and polylactic acid

2. The Fundamentals of 2D Enabled Smart Materials

This section focuses on the mechanism of stimuli responsiveness of ‘smart’ materials enabled by 2D materials, and the next sections will consider how these are integrated into devices through 3D/4D printing. In detail, the section is divided following the main properties of such materials: piezoresistivity, Joule heating, piezoelectricity, and shape memory polymers.

2.1. Piezoresistors

Piezoresistivity is the change of the electrical resistance of a material when a strain is applied. It is widely used in sensor applications. Piezoresistivity can be considered a stimuli response mechanism since mechanical stress (stimulus) triggers a change in the physical properties (i.e., the electrical resistance). Piezoresistivity is the phenomenon that enables strain sensing. Indeed, the most common feedback mechanism for determining the strain is the change of a conductor's electrical resistance when bent/compressed/stretched. The key parameter in strain sensing is the gauge factor (also called sensitivity) that represent the linear variation of resistance at a certain applied strain and is expressed as

\[ GF = \frac{\Delta R}{R_0 \varepsilon} \]

where \( \Delta R \) is the change in electrical resistance due to the applied strain \( \varepsilon \), and \( R_0 \) is the resistance when no strain is applied. Ideally, a strain sensor should have a GF as high as possible over a broad linear strain range.

Piezoresistive polymer nanocomposites have been studied widely due to their versatility and broad sensitivities achievable in response to strain. The mechanism of piezoresistivity is the formation and destruction of the electrically percolated network upon the external strain. The majority of printed matrix materials for this application have been elastomers, including natural rubber,[144] polydimethylsiloxane (PDMS),[145–147] and thermoplastic polyurethane (TPU).[148–150] as they can undergo considerable strain with elastic deformation upon the removal of external forces. The fillers in these nanocomposites have included carbon black, metal particles, and nanotubes. The past decade has also seen significant work on 2D fillers[144,151–159] due to their high electrical conductivity and aspect ratio.

Wu W. et al.[162] conducted a representative work on graphene-based conductive elastomer nanocomposites, which indicates the powerfulness of graphene to be used as a conductive filler in stretchable elastomers. They printed TPU and graphene/CB
nanomaterials with an excellent balance of features. The inks are prepared by mixing graphene and CB with different mass ratios in TPU. The inks are 3D printed, providing tunable electrical conductivity and elongation depending on the graphene-CB ratio. The performance is better than composites containing only one filler (i.e., graphene or CB), suggesting a synergistic effect between graphene and CB. Moreover, the conductors with binary fillers have constant electromechanical features for 1000 stretch/release cycles.

Fused depositing modeling was used by Zhang et al. [42] to print flexible circuits based on reduced graphene oxide (rGO). The printed filaments reached an electrical conductivity of 4.76 S cm\(^{-1}\) at 6 wt% r-GO concentration. The r-GO is oriented during the extrusion process, increasing the filaments' conductivity. The composite exhibited an improved Young's modulus while maintaining a strain at break of 6%. Printing such nanocomposites with different loadings of conductive nanofiller and structures can enable strain sensors with a tunable piezoresistive response with/on complex geometries/structures.

Aerogels incorporating 2D nanomaterials are also a practical approach for designing flexible piezoresistors. Aerogels are solid-state substances containing interconnected 3D networks and a high degree of porosity filled with air. Their structural and physicochemical characteristics bridge the nanoscale and macroscale, and they possess high porosity, large surface area, and low density. These properties mean that aerogels have excellent sensitivity, rapid response, and recovery for sensor applications.

In summary, the number of piezoresistive 2D material-based reports is increasing, indicating that 2D nanoplatelets are excellent candidates for strain sensors. Indeed, when blended with deformable materials (e.g., elastomers), they have generally high gauge factors (i.e., more than 10) at a strain that easily exceeds 20\% [164–165] which extends the detection range of metal/semiconductor-based sensors that usually cannot elongate more than 2–5\% [164,165]. Hence, it can be concluded that 2D nanomaterials, including graphene, TMDs, and MXenes, play a crucial role as conductive nanofillers inside polymeric matrices. The formation and destruction of the conductive network, rheological behaviors of the nanocomposites, and the orientation effect of the anisotropic nanofillers are the decisive parameters for the piezoresistive properties.

2.2. Joule Heating Materials

Joule heating is the production of heat by the passage of an electric current through materials. The Joule effect is an undesired side-effect in most electronics, such as in laptops and smartphones’ microprocessors. On the other hand, it is the basic principle for commonly utilized appliances such as hair dryers, toasters, hot plates, ovens, furnaces, and floor heating. The advantages of resistive heating are the ability to control heating uniformly, the simplicity of the power control, and the ability to concentrate high release of heat energy in a small volume. The heating behavior results from the scattering of the charge carriers with the atoms that constitute the material. The Joule heating is described by the formula

\[ P = I^2R \quad (2) \]

where \( P \) is the power (thermal energy generated per unit time) produced from the current, \( I \), travelling in the resistor, \( R \). Therefore, the potential difference applied to the resistor is the stimulus that create the heat due to the current flow. In this sense, Joule heating is a stimuli-responsive mechanism.

Due to their high electrical conductivity and their effective miscibility with polymers, 2D nanomaterials, such as graphene, and MXene, [169–172] have been introduced for such applications leading to extra stable and rapid heating. Indeed, graphene can be assembled in 3D self-standing structures or distributed homogenously inside matrices to offer a remarkable spreading of the heating spots. Therefore, 2D nanomaterials and their composites display great potential as nanostructured resistive heaters, and, thus, they are emerging as extraordinarily beneficial and favorable for the development of Joule heaters in many applications. 3D printing of such structures offers additional advantages in terms of versatility of the design and integration in existing technologies/structures.

For polymer-based (especially epoxy) structural materials, anti-icing could be achieved by implementing Joule heating. For example, Yang et al. [172] reported the preparation of epoxy resin nanocomposites filled with \( \text{Ti}_3\text{C}_2\text{TX} \) MXenes using an aerogel for low-voltage electrothermal heating. The unidirectional freeze casting led to the anisotropic MXene-based aerogel into which epoxy resin was then vacuum infiltrated and cured. The unique orientation of the conductive 2D materials contributed to an extraordinary Joule heating performance with repeated heating-cooling cycles. The as-obtained materials were prepared cost-effectively and offered a promising alternative route over traditional metal-based electrothermal materials. This technology could be exploited for anti-icing structures in airplanes or automobiles.

The Joule heating effect of polymer/2D materials composites can also be utilized for out-of-autoclave curing of thermoset polymers. Tian et al. [176] found that the Joule heating efficiently cured epoxy/GNP nanocomposites to give a more compact composite structure, fewer microvoids, and a preferred GNP orientation compared to conventional curing.

One of the latest works based upon the Joule heating effect on 2D nanomaterials is a novel controllable phase conversion of TMDs from 2H phases to 1T phases (Figure 2). The authors reported up to 76\% bulk conversion of TMDs from 2H to 1T, achieved within milliseconds by flash Joule heating. In the past, several methods, including ion-assisted chemical vapor deposition, strong magnetic hydrothermal treatment or ion intercalated methods, were developed to obtain 1T phase since it is a metastable phase, possessing high crystallinity and superior electrical conductivity. Among all the routes, the FJH is the most simple, fast, and effective way.

2.3. Piezoelectric Materials

Piezoelectricity is the electric charge generation upon external force or latent heat in specific solids (typically certain metals and ceramics) and polymers, or biological substances. The piezoelectric effect is reversible, indicating that materials showing direct piezoelectricity (electricity generation when stress is applied) also display the converse piezoelectric effect (the stress of a material when an electric field is present). Therefore,
2.4. Shape Memory Polymers for 4D Printing

Shape memory materials (SMMs) are defined by their characteristics of shape recovery from a quasi-plastic deformation upon particular stimuli.\[187–188\] In general, SMMs are categorized into shape memory polymers (SMPs), shape memory alloys (SMAs), shape memory ceramics (SMCs), and shape memory gels (SMGs).\[64\] At present, SMPs and SMAs are the most utilized SMMs. Superelasticity (in alloys) or viscoelasticity (in polymers) employ their shape memory effects (SMEs) under certain circumstances such as water immersion or heat/light administration.\[64,69,107\] Compared with SMAs, SMPs have gained growing interest in the recent past due to their low cost (≈0.02 € g\(^{-1}\) vs ≈0.45 € g\(^{-1}\)), high energy efficiency and processability (melting 100–300 °C vs >1000 °C), and excellent deformability (strain at break in the order of 100% vs < 8%; required stress for deformation 1–3 MPa vs 50–200 MPa).\[189–195\] Such features of SMPs make them promising candidates for 4D printing, and more recently, SMPs based on conductive nanofillers, endowing SMEs to the prepared nanocomposites, are frequently studied and discussed.\[69,196–202\] Most commonly employed SMPs are polycaprolactone (PCL), polytetrafluoroethylene, poly lactide, ethylene-vinyl acetate, polyurethanes, and (meth)acrylates.

In addition to thermal/electrical/mechanical responsiveness, photo-responsive SMP systems also attract attention since they can be developed into high-end applications in particular fields such as biomedical engineering.\[186,200\] Such materials are usually based on SMPs with good deformability to perform shape recovery in response to light. Conductive nanofillers (including 0D/1D/2D)\[200–201,203\] are usually employed in such materials to provide improved sensitivity to the stimuli, while it is always imperative to control the isotropy/anisotropy of the properties. The conductive 0D/1D/2D nanomaterials may be considered individually or as hybrids, depending upon the final application.

The light-responsive behavior depends on the chemical structure of the polymer chains, which may undergo photoisomerization, driving the materials to respond to external photon-based stimuli. Additionally, light-induced photo-thermal conversion may be a stimulus for shape recovery/change, exploiting thermally conductive fillers to enhance light-induced responses.

In a recent work proposed by Wang et al.\[201\] a bi-directionally reversible light-responsive SMP based on polyurethane (shape memory polyurethane, SMPU) was successfully prepared by a bilayer structural design, introducing azobenzenzoic acid (Azoa) on one layer and carbon black on the other. As can be seen from Figure 3, upon the exposure to ultraviolet (UV) and infrared (IR) lights, a reversible deformation was achieved by the SMPU-Azoa and SMPU-CB layers, respectively. UV-Vis absorption spectra were used to investigate the light-responsive bending of the SMPU-Azoa layer, and it was proven that the working mechanism was the reversible transformation of trans-cis photoisomerisation of SMPU-Azoa layer. On the other hand, the reversible light responsiveness of the SMPU-CB layer was due to the thermal radiation generated by the IR light.

A similar material design, utilizing photoisomerization, was reported by Chen et al.\[200\] aimed to mimic human muscles. The composite achieved a dual response to UV and near-infrared (NIR) light by introducing azobenzene and gold nanorods. Regarding the UV response, the azobenzene group
transformed from a thermally stable existing trans rod-like molecule into a cis V-shape molecule under a specific UV wavelength. From a macroscopic view, the materials presented effective bending deformation towards the UV light due to the shortened groups of azobenzene that induced accumulated internal stress. The energy stored in the molecular chains could react to the temperature increase, making the materials return to their original shape. In this work, the thermal energy was given by NIR radiation on the surface, which induced the plasmon resonance effect and led to the transformation of light to thermal energy by the Au nanocrystals. Owing to the extraordinary effectiveness of the sensing properties, the materials design shows promising potential in biomedical applications.

3. 3D Printed Stimuli-Responsive Materials including 2D Nanomaterials

The main applications for 3D printed stimuli-responsive 2D nanocomposites and 4D printed 2D nanocomposites are presented and discussed below. The available literature is grouped according to the target application. For stimuli-responsive nanomaterials, the main sections are strain sensing, Joule-heating, and piezoelectricity. For 4D printing, the most important works are on biomedical applications and actuators.

3.1. Strain Sensors

3D printed strain sensors are advantageous because of the simple preparation, low power consumption, and the myriad of printable geometries. Depending on the printing technique, the sensors can be freestanding or adhered to substrates or the body. A precise deposition practically on any surface permits a quick integration of such sensors and straightforward monitoring of its deformation. Therefore, 3D printing strain sensors enable ready-to-use devices. Electrically conductive 2D nanomaterials such as GRMs and MXenes, are excellent for strain sensing applications due to their intriguing electrical features and high aspect ratio. To date, GRMs are the most investigated for 3D printed strain sensors (see Table 1).

3.1.1. 3D Printing Piezoresistive Composites

Huang et al. employed direct ink writing to print graphene-PDMS strain sensors with ultrahigh sensitivity. The as-prepared sensors can tolerate 50% strain with small permanent deformation (≤5%). Depending on the different parameters of the printed filaments, such as diameters, interaxial angles, and interlayer spaces, a tunable gauge factor was achieved for 3D printed scaffold, as shown in Figure 4a, reaching a gauge factor as high as 448 at 30% strain in the best configuration. The graphene-PDMS sensor was successfully used to monitor human body motions, such as the subtle muscular movements in the throat and joints’ bending. Such a sensor’s performance was also tested in the compress-release configuration under 100 cycles at 10% strain, showing remarkable stability of the piezoresistivity under these conditions and looking promising for practical application.

Huang et al. undertook another study on the piezoresistivity of this system by adding polyvinylpyrrolidone (PVP) to fine-tune the viscoelastic properties and enhance the printability (optimal PVP loading was 0.51 wt%). This time, the graphene showed an aligned morphology, and the composite was shown to respond to various deformations such as bending, twisting, compressing, and stretching. The sensor showed a GF of 65 under 6% strain and was durable because it showed a 6% decrease in the response signal after 600 stretch-release cycles. The sensors proposed by the authors can detect human motion and gesture.

The same group designed a direct ink written structure printed on a flexible substrate and can detect bending according to the bend direction and GNP concentration. The ink composition in ethanol comprised ethylene glycol butyl ether as the dispersant and dibutyl phthalate and polyvinyl butyral as thickening agents (ratio of dispersant to thickening agent 1:4). The higher the 3D printed structure’s graphene loading, the lower the change of electrical resistance with bends, a trend in agreement with other literature. This behavior is due to the compact and well interconnected conductive nanoflakes network of the higher graphene content samples, preventing resistance change. The ΔR/R0 is anisotropic and is 0 along the X direction and is a maximum (≈2) at the bending radius in the Y direction, as shown in Figure 4b. When the bending is released, the initial value of resistance is restored. The same ink composition was printed with aligned GNP in a structure similar to...
the one presented previously in Figure 4a,[215] The alignment contributed to the electrical conductivity anisotropy of these graphene structures. Indeed, at a temperature of 450 °C, the electrical conductivities along with longitudinal and transversal graphene structures. Indeed, at a temperature of 450 °C, the electrical conductivities along with longitudinal and transversal directions of the 50 wt% loaded samples increased to 426 and 480 S m⁻¹, which are 8.4 and 6.7 times higher than ambient temperature, respectively. The piezoresistivity of these samples was tested under compression. The 50 wt.% loaded sample at 10% strain reached the best gauge factor of 25.

Recently, Wang Z. et al.[216] fabricated graphene-PDMS porous composites by direct ink writing. The composite had an electrical conductivity of 3 S m⁻¹ at 5 wt% nanofiller concentration. The authors used the printed filament arrangement to produce triangular, grid, and hexagonal structures to achieve a tunable piezoresistive response. Depending upon the design, the GF was in a range of 6–67 at a strain of 20%. The porous hexagonal assembly achieved the best durability of the sensors. This sample, over 100 tensile tests cycles at 20% strain, showed a resistance change in the stretched configuration of only ±8%, indicating the system’s relative stability, a requirement particularly relevant for implementation. The sensor could detect each finger’s motion by providing a distinct but controllable change in resistance at the same strain depending on which finger was tested. As a result, the authors claim that this sensor is promising for various functions, including a wearable musical instrument.

SLS is emerging as a convenient technique to 3D print strain sensors in a single step due to the powdered forms of GRMs and polymers. For example, Ronca et al.[217] used SLS to print electrically conductive TPU-graphene porous structures. Different structural designs and porosities were achieved, as shown in Figure 4c. The Schwarz geometry of the porous structure exhibited the highest elastic modulus. Upon 50 cyclic compress-release cycles at 8 % strain, all the designs displayed a negative piezoresistive response. A GF of −12.4 at 8 % strain was reached at 40 and 60 % porosity, demonstrating the feasibility for the SLS manufacture of strain sensors with good repeatability. The same authors recently demonstrated that SLS could be used to realize a porous composite of TPU with a hybrid mixture of MWCNTs and GNPs.[218] Such hybrid structures exhibited improved properties compared with a single filler, showing a negative GF of −13 at 8% strain. Another strain sensor made of a hybrid of MWCNT-GNP (total nanocarbon loading of 2 wt.%) and TPU was produced with FDM by Xiang et al.[219] In this study, the MWCNT/TPU nanocomposite exhibited a GF of 5.67 at 30% strain, while the GNP/TPU nanocomposites showed a remarkable sensitivity (GF of 67.31 at 30% strain). The MWCNT/GNP nanocomposites displayed a GF = 31.82 at the strain of 30%. Repeated stretch release cycles at 50% strain (3000 cycles) showed that the hybrid strain sensor was the most durable due to a lower hysteresis than the single filler composites.

Jakus et al.[220] direct ink wrote scaffolds for tissue engineering made of graphene and polylactide-co-glycolide with up to 60 vol% of conductive particles and a high control in the diameter of the filaments that can range from 100 to 1000 µm and electrical conductivity of 800 S m⁻¹. The 3D-printed filaments with a diameter of 400 µm changed the electrical resistance by a factor of 10 at an applied strain of 20%, which corresponds to a GF of ≈50. Cyclic bending at a radius of curvature of 6.5 mm exhibited a dependence on the fiber diameter. Indeed, the fibers with small diameters (i.e., lower than 400 µm) displayed constant features upon 1000 bending. The authors suggested that filaments had potential applications in tissue engineering, implants, wearable electronics, and sensors, particularly given that the smaller diameter fibres maintained their electrical conductivity through repeated bending cycles. To establish their potential in implants, human mesenchymal stem cells were grown in vitro on the filaments, and neuron-like morphological characteristics were observed.

### 3.1.2. 3D Printing Piezoresistive Aerogels

Carbon-nanomaterial-based aerogels have unique features such as large surface area, low electrical resistance, low density (<10 mg cm⁻³), and good mechanical properties, not commonly obtainable in most aerogel structures.[224,225] Such aerogels showed that they could combine the detection of both strain and force over a broad range of deformation (>50%) and pressure (tens of Pa to hundreds of kPa),[226] respectively. Therefore the 3D printing of such gels can be convenient for piezoresistive sensors.[227,228]
Figure 4. How the design of a 3D printed structure can change and influence the Gauge Factor of a strain sensor. a) Design diagram of the 3D printed GNP-PDMS filament with parameters, D: diameter of filaments, θ: interaxial angle, and L: interlayer space. In the coloured box, the gauge factor as a function of strain with different filament diameters (0.3, 0.4, 0.5 mm; red), interaxial angles (30°, 60°, and 90°; green), and interlayer spaces (0.35, 0.4, and 0.45 mm; blue). Reproduced with permission. Copyright 2019, Elsevier. b) Left: schematic of a circuit made of ethylene glycol butyl ether as the GNP dispersant and dibutyl phthalate and polyvinyl butyral as thickening agents (ratio of dispersant to thickening agent 1:4) printed on a flexible substrate Right: change of the circuit’s electrical resistance with 25 (black) and 50 (red) wt.% graphene loadings under various bending radius. Reproduced with permission. Copyright 2018, Elsevier. c) Left column: schematic of the different CAD-design for the selective laser sintering of GNP-TPU composite; Center column: CAD-designs of 3 × 3 × 3 assembled structures; Right Column: photos of the TPU/GNP composite after fabrication. Reproduced with permission. Copyright 2019, MDPI, Basel, Switzerland.
An et al.[223] fabricated GO paste with concentrations from 5 to 25 mg mL$^{-1}$, which were then directly written onto PET substrates and vacuum freeze-dried to form the GO aerogels (Figure 5). Afterward, they reduced the GO chemically to improve the electrical conductivity. The reduced GO aerogel was encapsulated into PDMS to obtain a graphene aerogel sensor which was tested under compression up to a maximum stress of 3.29 MPa, getting a maximum resistance change of 111% for the 15 mg mL$^{-1}$ concentration in the inks. The electrical resistance was tested over ten compression cycles at 20% strain with a maximum $\Delta R/R$ of $R_{\text{initial}}$. The same aerogel was subjected to a tensile test and showed an increase in the resistance of 558%. The GF was reported to be 5.2 at 2% strain. This system showed good repeatability under 1000 cyclic bending to 90°. The aerogel was used to detect gesture language for the ultimate application of deaf-mute communication devices.

Zhang et al.[222] directly wrote GO-based inks that were reduced and freeze-dried to create an aerogel. Their structures were ultralight with a density ranging from 0.5 to 10 mg cm$^{-3}$ with a conductivity of 2.2–15.4 S m$^{-1}$, depending on the graphene concentration in the inks. The electrical resistance was tested over ten compression cycles at 20% strain with a maximum $\Delta R/R$ of 26% and a linear GF of 1.3.

### 3.1.3. 3D Printing Graphene on Bendable Substrates

3D printing is a versatile technique for functionalizing bendable/stretchable substrates with conductive paths that function as strain sensors. Such an approach has the advantage of a simple implementation in existing technologies. Maurya D. et al.[224] directly 3D printed rGO strain sensors on Kapton on tires to measure their interaction with the asphalt during vehicle movement. The graphene printed sensor was obtained by five passes of the desired geometry to give a total thickness of ~10 μm. These piezoresistive sensors were integrated on a tire to measure the deformation with vehicle motion. The authors measured the change in resistance in a bending configuration showing a linear change in resistance till 0.7% strain and a GF of 1.7. Such work demonstrates a possible application of 3D printed strain sensors that are easily integrated into existing technology and have a reduced production cost (the authors estimated $0.027 as the price of one sensor).

### 3.2. Joule Heaters

Yao et al.[230] direct ink wrote graphene oxide in the desired shape (see Figure 6a) and then reduced the printed structure through Joule heating. The 3D printed heaters could reach a heating temperature of 3000 K (1500 K with 4 V bias voltage) and were activated through voltage control at high switching rates, up to ~20 000 K s$^{-1}$ for 2000 cycles without performance deterioration. The authors used these rGO structures to melt metal particles. The authors claim that this heat source is advantageous compared with conventional infrared, furnace, or laser heating since it can reach an extremely high temperature at a fast rate. It can be printed directly onto different substrates with an arbitrary shape with a resolution of 100 μm. Therefore, it can be applied to many manufacturing processes when accurate and fast temperature control is needed.

Guo B. et al.[221] 3D printed a heater through direct ink writing water-based nitrogen-doped graphene nanosheets, CNTs and flour. This heater responded well with applied voltage heating at 89.5 °C under 20 V tension and 44.6 °C at 12 V in less than 2 minutes. The temperature buffering property was remarkable, exhibiting a cooling rate of 0.1 °C s$^{-1}$ from 89.5 to 35 °C due to water presence. The heater was self-healable, stretchable, and biodegradable. Indeed, the heater was healed ten times after cutting and was stretched with minor performance change, as shown in Figure 6b. The healed heater temperature did not change significantly under bending conditions (100 bend cycles, Figure 6b). The authors claim that soil and gastric fluid could dismantle this heater in 20 and 8 days, respectively.

Cortés et al.[213] 3D printed conductive inks made of epoxy and GNPs/CNTs hybrids for seat-heating and de-icing systems. The optimized sample for anti-icing/de-icing was found to be an epoxy ink doped with 2 wt% GNPs and CNTs. Applying a 1000 V on a diamond-like geometry 3D printed circuit (Figure 6c) meant that a thick ice layer of 2.65 mm could be removed in 3 min and 30 s. The same authors also found a similar system of materials to work as structural health monitoring feedback.[174]

### 3.3. Piezoelectric Devices

The possibility to print piezoelectric composites with on-demand shapes through 3D printing is relevant. The addition of conductive nanofillers to such piezoelectric structures significantly improves poling, the process that permits orienting and aligning the Weiss domains of the ceramic particles by applying an electric field during fabrication and improving the final piezoelectric features. Such a strategy was used by Jin Y. et al.[213] that report the 3D printing of a polyamide 11/barium titanate (BT)/GNP ternary nanocomposite with considerably enhanced piezoelectric features due to its graphene network. Piezoelectric BT nanoparticles were dispersed into...
the polyamide via shear milling and blended with GNP using bath sonication and filtration. The obtained powder was selective laser sintered to print the nanocomposites. The graphene acted as electrodes and thus significantly increased the poling efficiency. As a result, a piezoelectric coefficient $d_{33}$ of 3.8 pC N$^{-1}$ was obtained. The authors claim that their work led to high-performance piezoelectric materials fabricated through a convenient 3D printing method that discloses new configurations and designs in piezoelectric materials.

4. 4D Printed Materials Comprising 2D Nanomaterials

4D printing needs structures that are dynamic and evolve with time upon a triggering stimulus. Therefore, it needs smart materials that can change shape. Shape-memory polymers (SMPs) are among the best candidate for this task, as detailed in section 3. Hence, they are promising in usages such as sensors, actuators, and drug delivery. Enriching SMPs with...
2D nanomaterials and GRM can improve their physical and chemical properties and impart new ones. Thus, SMPs with GRMs present superior features to traditional SMPs, such as more triggering strategies, remote control opportunities, and faster response speed. This behavior is due to the GRMs excellent electrical/thermal conductivity and the photo-thermal conversion capacity of these nanomaterials. Electrical, thermal, and light stimulation is the most commonly used trigger to enable shape changes. Changes in pH, solvent (e.g., water/ alcohol), and the presence of metal ions can also be utilised to trigger SMPs with GRMs.

Another excellent alternative to achieving 4D printing is assembling multimaterials arranged to transform with the appropriate stimulus over time. For example, successful strategies use the diverse swelling of material upon contact with a liquid or the different thermal expansion coefficients. GRMs are the right candidate for this latter purpose since they can be heated up simply with an applied voltage using the Joule effect. However, the dynamic/multimaterial are assembled plays a crucial role in achieving a specific functionality (e.g., dynamism due to swelling after immersion of the printed structure in a liquid). Adding 2D nanomaterials can help activate the 4D printing mechanism or enhance its range of dynamics. An optimized material distribution can significantly benefit from computational modeling to control and predict the final material’s behavior. Such a simulation step implies the programmability of the final 4D printed structure. Various tools for modeling and selecting materials distribution were reported, such as structural lattice criteria, multiple-material topology, and dynamic rod structures optimization. Another method is the voxel-based modeling strategy based on a CAD modeling software such as Rhinoceros© and a graphic algorithm editor such as Grasshopper. A recently proposed approach that reduced the difficulty of modeling the non-linear behavior of smart materials and nanocomposites was proposed. In this approach, an empirical model predicts the kinetic components’ motions. The authors claim this empirical method is preferable when existing numerical methods are ineffective and computationally expensive. With this method, the authors can consider more motions, including torsion, whereas previous studies only considered simple hinge folding.

The following section will review the work related to the 4D printing of materials comprising 2D nanomaterials that employ SMPs or a structured assembly of constituents that become smart. The works are presented starting with improvements to existing SMPs due to the inclusion of 2D nanomaterials, their biomedical applications, and actuators’ application.

### 4.1. Shape Memory Polymers Improved with 2D Materials

Guo et al. 3D printed stretchable graphene hydrogels and, after a freeze-drying and annealing step, obtained an aerogel that was infiltrated with polycaprolactone solution. The final result was a film of SMP coated on the graphene network that displayed a fast response of up to milliseconds scale, comparable with state-of-the-art shape memory alloys. The high thermal conductivity of graphene coupled with the nanometric thickness of the SMPS allowed achieving an extremely short heat transmission distance, enabling a 50 ms response at a low electrical field of 0.1 V mm⁻¹ (~0.5 W mg⁻¹), as shown in Figure 7a. This structural design extends SMPS recovery time limit and provides a practical approach for achieving SMPS composites with fast response and large deformability up to 100% elongation. The authors claim that the 3D printability, which allows freedom in designing the final structure, together with the stretchability and the fast response, provides vast opportunities for such shape memory material in microrobotics and smart devices in general.

Xu et al. have recently investigated an epoxy/graphene oxide (GO)/CNT SMP-based nanocomposite system, where the addition of the conductive hybrid fillers improved the thermal response of the composite with low strain and alleviated the mechanical relaxation. With the addition of up to 4 wt% fillers (2 wt% CNT and 2 wt% GO), the thermal response recovery rate of epoxy was significantly improved under 10% strain. At 10% pre-strain, the maximum thermal response recovery rate of the composites filled by hybrid fillers (CNT and GO) was 57%, 158%, and 22% higher than that of the pristine epoxy, GO/epoxy composites, and CNT/epoxy nanocomposites, respectively. The combination of 1D/2D conductive fillers improved the thermal response recovery of the nanocomposites and piezoelectric properties since the percolated network can be enhanced by increasing the contact area of the two different fillers.

Thermosets such as epoxy can be employed in 4D printing by a novel fused deposition modelling, unlike conventional FDM that only involves melting extrusion and deposition followed by cooling to form a 3D structure (typically for thermoplastics). Chen et al. achieved an FDM 3D printable thermosets/CNT/graphene system thermally responsive with a fast recovery rate (Figure 7b). The material was constituted of epoxy, benzoxazine, graphene, and CNT to form a hybrid resin mixture that behaves as a low-temperature thermoplastic and a high-temperature thermoset, where nanomaterials were used to tune the rheological properties to adapt printing. Therefore, the system can be printed at low temperatures into complex structures and cured at high temperatures. The highly-crosslinked materials contain deformable linear chain segments that offer the samples shape memory properties, enabling the prepared materials to respond rapidly to thermal conditions.

### 4.2. Shape Memory Polymers for Biomedical Applications

SMPs such as PCL and polylactide possess desirable properties for biomedical applications such as biodegradability and biocompatibility and also have the typical advantages of polymers such as low cost, large deformation, and lightweight. The usage of SMPs in biomedical applications could enable dynamic devices that can be introduced into the body of a patient in a temporary shape that evolves and reprograms on demand. A particular shape can be achieved by simply changing temperature, allowing controlled responses to be triggered, and giving the possibility to realize devices such as micro-actuator for stents. Furthermore, such dynamic structures are ideal for true biomimicry of living tissues, and 4D printing could enable ready-to-use structures that could substitute old/damaged
Temperature is one of the most common mechanisms for shape control, especially in biomedical applications. Nevertheless, filling such polymers with nanomaterials can deliver shape control under diverse stimuli such as magnetic, mechanical, or electrical. Thus, SMPs can become multiresponsive and multifunctional, enlarging their range of applications.

State Miao S. et al. | Advanced Materials Technologies (2022) 7, 2200025. 4D printed soybean oil epoxidized acrylate, which is a photocrosslinkable monomer. The curing of the polymer was controlled with laser light. Stress-induced shape transformation was achieved depending on the curing parameters and upon solvents immersion. This 4D printed effect was amplified and controlled using graphene, developing specific needs for diverse applications. Indeed graphene acted as a photo absorber to control laser penetration. Indeed, the printing ink exhibits significantly decreased light penetration when the nanoparticles are added. For example, the authors show that by varying the content of nanoparticles in the inks, a bird with a series of flying actions was easily generated after the 4D printing (Figure 8), indicating that the curvature after curing can be tuned by varying the nanoparticle concentrations. The addition of graphene hinders laser penetration through the ink, leading to a weak cross-linking effect. The authors...
demonstrate that this multiple responsive 4D printed material is adapted to fabricate nerve guidance conduit (Figure 8), providing exceptional multifunctional features for nerve regeneration such as chemical cues, self-tubulation, physical guidance, and simple integration.

Cui et al. [203] 4D printed an SMP epoxy nanocomposite with graphene that was NIR light-responsive. Such shape memory composite was activated by the NIR light absorption of graphene that produced thermal energy. When the thermal energy caused a temperature higher than the glass transition temperature of the SMP, the object transformed its shape. The authors claim that such a strategy ensured a higher control than direct thermal control and was a precise, remote, and tunable control in time and position. Moreover, NIR light can safely penetrate human tissues. The authors show how light enables the shape transformation of diverse printed objects, including a model brain and a dilated heart. They proved that the 4D printed constructs exhibited outstanding neural stem cell differentiation and growth, paving the way for the employment of such materials for biomedical applications.

4.3. Actuators

Actuators are devices that convert diverse forms of energy into mechanical movements through a control signal (input). The inputs that produce the mechanical action are electric (typically an applied voltage or a current), hydraulic (liquid flow/movement), pneumatic pressure (compress air/vacuum), light, or heat-induced, as shown in Figure 9a. Industrial actuators are, for example, electric/hydraulic motors and pneumatic control valves. Examples of actuation that can be appreciated daily are automatic doors, car seat movements, cell phone vibration, and electric toothbrushes, to cite a few. Actuation can be linear (moving something along a straight line) or rotary (circular motion), as schematically drawn in Figure 9b. In light of the predictable movement depending on the material design and the control through a stimulus, actuators could benefit significantly from the 4D printing technology. In particular, printed soft actuators made of elastomers/hydrogels are believed to be very promising to breakthrough sensing/motions in soft robotics and enable the mimicking of human muscles. [241–242] 4D printing could simplify the actuators' manufacturing procedures and permit printing ready-to-use ones with tunable/controllable movements. Furthermore, adding 2D nanomaterials such as graphene to 4D printed actuators can provide new functionalities, enhance the actuation in terms of time response, and enable/improve the motion's electrical control. The 4D printing of 2D nanomaterials for actuation is still limited but inspiring.

4.3.1. Polymer-Based Actuators

Coupling polymers with nanomaterials was found to be convenient for actuation compared with metal-doped actuating plastics. [245–246] This approach is promising for bio-mimicry due to the lightweight, easy processing, and mechanical flexibility of many polymers. [245–246] Furthermore, some polymers display significant variations in response to electrical/chemical stimulation, much more significant than what is attainable by inorganic materials. [246] Therefore, their application in actuators is valuable, especially in composites enriched with nanomaterials that provide/improve new/their features.
Figure 9. a) Possible input responsible for actuation and b) schematic of the different kinds of actuation. c) Left: production of a conformable polymer-based actuator with 3D-printed rGO electrodes. Schematic of the rGO/PDMS layered structure and its actuation under electrical stimulation. Right: maximum actuation angle as a function of the applied voltage. Photos of the actuator at different bending angles and times. Hand-shaped actuator and various movements by independent control of the fingers. Reproduced with permission.[243] Copyright 2016, American Chemical Society. d) From left to right: Schematic draw of the direct ink writing of the hydrogel made mixing GO with sodium alginate, the printed microscopic structure and the printed lines, and the atomic composition of the composite and the assembly of the GO after drying. After the collapse, followed by the water evaporation, a brick mortar structure is achieved. Reproduced with permission.[244] Copyright 2020, Wiley.
Li et al.\textsuperscript{[241]} utilised direct ink writing to print GO. They claimed that the shear force exerted on the flakes during the printing process induces the alignment of the GO. After chemical reduction, the rGO achieved an electrical conductivity of $4.6 \times 10^4$ S m$^{-1}$. Uniform and large-area shapes were printed on flexible PDMS substrates. The graphene electrodes were stable under multiple bending cycles and suitable for electronically-driven soft actuation (Figure 9c). These rGO/PDMS structures’ actuation was based on the asymmetrical swelling/contraction induced by the Joule effect under an applied voltage. The rGO is the active component (electrode) that heats up upon current flow, while PDMS is the passive layer that deforms when the voltage is applied. The authors claim that, since graphene has a negative coefficient of thermal expansion while PDMS has a positive one, the rGO-PDMS bilayer structure produces a motion due to the two materials’ asymmetric expansion. The bilayer bends towards the rGO side when heated due to an applied voltage. The actuators’ maximum bending angle increases with the input voltage and is higher with a shorter device length. Reversibility of actuation is shown for the shorter actuator under an applied voltage of 13.5 V. This actuator needs 5 s to reach the maximum angle at 300° and 9 s to come back to the initial position.

De Maria et al.\textsuperscript{[248]} 4D printed a tendril-like structure through a one-step procedure, which constituted of an internal wire of biocompatible graphene nanoplatelets (GNPs)-modified regenerated silk and an external shell of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). They obtained torsional and contractile actuators because the different coefficients of thermal expansion of regenerated silk and PHBV succeed in transforming thermal energy into mechanical contraction and torsion. The fabricated structure can self-twist and contract as an artificial muscle, increasing temperature, and humidity. The described capabilities were enhanced by introducing GNPs inside the silk matrix.

### 4.3.2. Hydrogel-Based Actuators

In light of their softness, stretchability, conductivity, and self-adhesiveness, hydrogels are seen as promising for actuation that involves small mechanical stresses (few MPa or less) and when the adhesion of the actuator is pivotal. For example, they are particularly suitable for epidermal actuators/sensors for human-machine interaction or wearable technologies.\textsuperscript{[249–250]} Indeed, they can avoid using bandages or tapes for the adhesion on the skin/substrate and can easily comply on curved surfaces at a micrometric scale.\textsuperscript{[249]}

Since hydrogels contain high water content, GO, which is hydrophilic, is ideal for realizing gels that are 4D printable and can be used for actuation.\textsuperscript{[251]} Zhang et al.\textsuperscript{[244]} printed GO sodium alginate nanocomposites with aligned flakes due to the shear force exerted on the nanoparticles when being extruded from the nozzle. After drying on a substrate, the printed materials formed a brick and mortar structure due to a synergistic effect of the gravity and confinement of the substrate (Figure 9d). This structure was responsible for the anisotropic deformation of the material upon stimuli activation. Depending on the printing pathway, the alignment of the GO could be finely tuned to obtain either bending or twisting. Finite element simulation was used to design and tune the morphing architectures rationally. The 4D printed composites exhibited a fast response (in the order of seconds) to different stimuli, comprising heat, light, and water vapor. In particular, reversible actuation can be achieved using water vapor.

### 5. Conclusions and Future Perspectives

3D printing is a technique already available on a large scale and is forecasted to become even more pervasive in the industry and the public. This technique’s strength relies on combining a design stage achieved through user-friendly software and versatile and straightforward printing processes. Enlarging the library of printing materials to deformable and stimuli-responsive ones promises to give further momentum and importance to the 3D printing sector. Indeed, in the short term, it will enable the printing of ready-to-use piezoresistive sensors or dynamic structures that evolve in a programmed way after stimuli activation, such as 4D printing materials. Simultaneously, coupling such smart materials with nanomaterials could improve their dynamic response and/or give new functionalities.

The 3D printing of smart materials and 4D structures enabled by 2D materials is still at an embryonic stage but promises to drastically simplify how to obtain functional materials and give a boost to the mimicry of living tissue and the prototyping of soft robots that are similar to humans. The main challenge for effectively printing dynamic structures is balancing 2D material loadings, stimuli response, and effective printability. This review shows that 3D/4D printing active materials employing 2D nanoparticles will impact strain sensing, Joule heating, piezoelectric materials, and actuators, as shown in Figure 10. The research of solutions to enable ready-to-use printed material has made some advancements in these applications. For example, printing polymer-based composite made with elastomers and graphene or with 2D materials-based aerogels were the main approaches used to achieve ready-to-use piezoresistive sensors with gauge factors higher than metal/semiconductor-based sensors and at higher strain. The printing of graphene-based heaters showed promising results, permitting to obtain Joule heaters that can reach a high heating temperature of 3000 K that can be activated through voltage control at high switching rates. Another sector that made exemplary achievements is the 4D printing of materials for biomedical applications. In the short term, such technology could enable the printing of implantable and motile materials, and in the long term, it could enable the substitution of damaged organisms/organisms. 4D printing actuators with applications in diverse areas is also a sector that was investigated, showing encouraging results and reaching good outcomes with polymers and hydrogels. These materials are promising due to the lightweight, easy processing, and mechanical flexibility of many polymers that enable lighter and easy-to-build actuators in many sectors such as soft robotics.

Despite the described advances, 3D printing smart and 4D structures enabled by 2D materials remain underexplored avenues for the fabrication of multifunctional, programmable smart structures/devices. So far, the literature has focused
mainly on using GRMs since these are already available at the scale needed for 3D printing and are cheaper than the other 2D nanomaterials. To further develop stimuli-responsiveness and 4D printing, research on new material combinations is needed to optimize the shape's control of the dynamic printed materials' size and topography. The control over the shape change and the hysteresis of such mechanical deformation also needs further improvement. Regarding 2D nanomaterials, there are challenges and opportunities in changing the rheology and the properties of the printing materials, considering the enlarging of the 2D nanomaterial family much beyond graphene. In the field of materials for biomedical applications, the degradation of the scaffold employed could constitute an excellent advantage for a transient application. Using multimaterial printing and smart materials enriched with 2D nanomaterials is a promising way to tackle the issues still present for printing dynamic structures and enabling new functionalities. With this respect, MXene and hexagonal boron nitride are still under-investigated but could give excellent results considering their chemistry and features differences compared with graphene and the different rheological properties and interaction with polymer matrices.

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Figure 10. Schematic summarizing various dynamics mechanisms achievable with 3D printing and 2D nanomaterials. The dynamism of the structure is achieved through 3D printing smart (red) and 4D (blue) structures enabled by 2D materials. The schematic of the two distinct concepts of 3D printing stimuli-responsive materials and 4D printing is highlighted. The first prints a material that utilizes a stimulus to modify the properties/shape; the second prints programmable structures, meaning they change properties/shape depending on time and predictably after stimuli activation. It is shown that, if carefully designed and optimized in terms of material combinations, shape's control of the dynamic printed materials' size and topography, these new classes of 3D printed materials could improve 3D rigid structures giving dynamism and enabling new functionality such as electrical conductivity, thermal conductivity, and piezoelectricity to enrich the dynamic structures with new possibilities and applications in strain sensing and joule heating. Furthermore, these techniques will enable the prototyping of ready-to-use components for diverse applications such as actuators and shape memory polymers for biomedical applications. When optimized ink formulation and printing processes are achieved, perspective use of these techniques is envisioned in soft robotics and advanced motile prosthesis.
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