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Study on Polymer Intelligent Materials and Actuators Based Graphene

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ABSTRACT

The invention relates to an actuator for graphene oxide humidity response, and graphene has become a growing material in developing electronic devices due to its unique physical and chemical properties. For intelligent materials used in soft actuators, fast response and strong mechanical properties are required. The invention relates to the field of 4D printing of intelligent materials. Specifically, it relates to a field in which a shape-memory micro-nano composite material can be applied to 4D printing technology. The purpose of the invention is to solve the technical problem that 4D printing of shape-memory micro-nano composite materials is difficult to achieve. 4D printing technology has played an essential role in promoting the development of graphene materials as devices. This article reviews the research progress on the 4D printing of graphene in sensors and actuators. Also, it provides a creative idea for investigating novel soft actuators through the combination of responsive nanocomposite and stimulus programming. The advancement of 4D printing graphene materials in sensors and actuators is explained in detail, and the prospects for further research and use of these materials are concluded.

1. Introduction

Intelligent materials will be the primary concern because the fourth dimension in 4D printing refers to the ability of material intentions to change form and function after they are generated. Many have cited intelligent materials as a significant technological advancement, enabling endless possibilities for fictional items [1]. Using intelligent materials in additive-layered manufacturing (ALM) technology is one of the most effective ways [2]. Actuators are promised for cutting-edge applications in microfluidics, robotics, aerospace, and biomedical science as a critical component for future smart apparatus [3]. Due to its distinctive, idiosyncratic properties and structural features, graphene, a two-dimensional compositional material for carbon materials of all other dimensionalities, is emerging as a rising star in material science [4]. Using innovative polymer-based materials has generated considerable interest in these printing processes [5]. Polymers have various benefits for technologies utilizing printable intelligent materials, including low cost, greater versatility than inorganic materials, and greater flexibility [6]. Creating intelligent interacting polymers is entirely at odds with the conventional method. The polymers used to develop intelligent materials must be able to interact with and react to the surrounding chemical environment specifically. Innovative materials must be able to initiate the proper chemical reactions when necessary. Chemical property control

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makes it possible to create polymers with selective interactions. [7]

The next generation of printing techniques used novel materials to produce structures that could alter shape over time. The static aspect of 3D printing is the primary differentiator between it and 4D printing. 3D printing (AM) is used in 4D printing to create stimulus-responsive active materials that change physically or chemically over time. A 4D printing procedure generally employs a printing technique to create structures that can adapt to inputs by actuating an intelligent material [8]. Due to its revolutionary utilization of energy and reduction in volume, 4D printing could be applied to biological applications. A recently created Close-infrared Receptive (CIR) 4D composite made of photothermally responsive graphene and thermally sensitive shape memory polymer composites (SMPCs) [9]. An actuator is a mechanical device that responds to a suitable external stimulus to move or regulate a mechanism or system. Actuators are an energy conversion system that transforms external energy into mechanical energy. Inorganic compounds, polymers, and carbon-based materials are frequently used as actuator materials. As a stable 2D material with a single atom layer, graphene possesses several intriguing qualities that make it a potential contender for actuation materials. It is highly sought as a high-performance actuator material due to its superior electrical and thermal conductivity, high surface area, super mechanical strength, and increased flexibility. Various actuator materials have multiple advantages and restrictions [10]. Polymer actuators can change their shape in response to changes in applied signals, such as electrical or magnetic inputs, or environmental factors, such as temperature or pH. Actuators include, but are not limited to, shape memory alloys, piezoelectric ceramics, electroactive polymer (EAP) actuators, electronic and ionic actuators, magnetoactive, electrostatic, and ferrofluids. Designers can construct sophisticated actuators for handling more significant things and soft actuators for manipulating soft living tissues since polymer materials can be either hard or soft depending on their chemical and physical nature [11]. Materials like graphene and their relatives have become intriguing prospects for creating many types of electrical devices, such as supercapacitors, photodetectors, sensors, and actuators. Due to improvements in preparation techniques, graphene and its derivatives are now successfully used in various stimuli-responsive actuators, demonstrating their enormous promise for applications in soft MEMS, bionic robots, adaptive optics, and motion perception [12]. However, pristine graphene's limited chemical activity and issues with mass manufacture severely limit its potential for use. A non-conductive but hydrophilic substance is graphene oxide (GO), which has abundant oxygen-containing groups on its graphene lattice (such as carboxyl, carbonyl, and hydroxyl). Many aqueous solutions can quickly disperse GO, and it exhibits strong interactions with various guest molecules, suggesting significant prospects for cutting-edge applications, including sensors and actuators. Actuators, a crucial part of the intelligent system, can be grouped according to various stimuli, including light, moisture, electricity, solvents, pneumatics, etc. Consequently, graphene has gained popularity as a potential host material or addition for light-driven actuators [13]. Recently, graphene, an allotrope of carbon single-layer atoms with a two-dimensional hexagonal lattice nanostructure, has been shown to fabricate properties for high-performance actuators [14]. Electroactive polymer (EAP) actuators have several excellent properties, such as an impressive energy conversion rate, high toughness, vibration reduction, fast switching response, and high strain in bionics. However, cellulose acetate (CA)-based EAP actuators show relatively low bending properties [15-16]. Ionic polymer-metal composites (IPMCs) are distinctive EAPs that may bend softly when driven at low voltages [17]. Intelligent materials made of polymers offer good elasticity, lightweight, and high transparency advantages but weak mechanical strength, delayed response, and terrible environmental stability disadvantages [18]. In actuator production, Nafion is the most widely used; however, the degree of actuation in pristine Nafion could be more desirable. The actuation level will increase by reinforcing with graphene and developing a high-performance composite. [19]

This study reviews polymer intelligent materials, their bioinspired smart actuator, a soft actuator mechanism, chemically, electrically, thermally, magnetically, and photo-responsive properties, and intelligent materials for structural and functional applications. We also review developments in the soft actuation of 3D printing technologies. We first review typical 3D printers and their use of graphene and polymer composite-based soft actuators. Then, we describe recently developed AM (3D printing) applications in greater detail, such as their structural and functional uses in biomedical, soft grippers, sensor-integrated soft robots, and wearables. This study aims to offer a more comprehensive analysis of this area and concentrates on its capabilities and applications.

2. Additive manufacturing technologies

The term "additive manufacturing technology" refers to a scientific and technological technique that uses the discrete-accumulation principle to create products directly from three-dimensional data of the parts. The terms quick prototyping, rapid manufacturing, 3D printing, etc., are just a few of the names given to additive manufacturing technology based on various classification systems and modes of thinking. Its extension is continually growing, and its connotation is still deepening. The terms "rapid manufacturing" and "rapid prototyping" are interchangeable when referring to the "additive manufacturing technology" that is addressed here. In additive manufacturing, software often transforms a CAD item into a 3D printable design. Sending this file to a 3D printer will allow the material to be placed layer by layer until the desired thing is created. Traditional 3D printing materials include food, metal, liquid resin, and plastics like PLA and ABS. A 3D printer transforms a computer design into an actual product in a "digital to physical conversion." A material (often filament) is applied to a print bed through a nozzle in a series of layers using a more conventional FDM printer. UV light solidifies liquid resin into a solid in a resin-based 3D printer. A different additive manufacturing technique (Fig 1) is metalworking, which involves melting metal-based powder in layers to create a solid. [20-21]

2.1. Soft actuation of 3d printing technologies

A multi-material 3D-printed development with soft and rigid segments is the basis for creating a soft actuator [22]. Soft robots are now easier to design and can be made more quickly because of advances in soft material 3D printing [23]. Soft actuators are made of molecular integration, which causes microscopic deformation of actuator materials by its driven stimuli like light, thermal, electric, and pneumatic. For existing actuators, materials must be fabricated using rapid prototyping technology such as 3D printing [24]. Extrusion of materials, which includes fused deposition modeling (FDM) [also known as fused filament fabrication (FFF)] and direct ink writing (DIW), vat photo-polymerization, powder bed fusion, and material jetting, are the five 3D printing techniques that are most frequently used for soft actuator applications [25–26]. Table 1 compiles information about the workings of each 3D printing technique, the materials used to make soft robotics, and the various types of soft robots produced using each method. 3D printing, also referred to as additive manufacturing, revolutionizes traditional manufacturing layer-by-layer, creating 3D objects using data from 3D computer models and computer-controlled translation processes. The availability of more than 50 different 3D printing processes, each of which meets a different set of needs, makes the technology flexible with enormous potential for advanced manufacturing in the future [27]. Soft actuator materials are 3D printed using patterning and curing in three dimensions.

Table 1. Lists the 3D printing processes utilized to create soft robotics. [25]

3D printing techniques	3D printed materials	Typical design	Actuation method
FDM or FFF	TPE filament made from SMP	Tubular gripper Fingers-like grippers	Pneumatic
DIW	Elastomer Silicone	Tubes Simple 3D constructs	Pneumatic Electric Magnetic
Vat polymerization	Hydrogels (PEGDA) Elastomer-like resins Silicone	Tubular grippers Beam-like grippers	Pneumatic Other activating layers such as residual stress from cell sheet Light-actuated
Powder bed fusion	PU92A-1 PA12	Multi-arm snake-like kinematic structure Multi-fingered hand	Pneumatic Bowden wire
Material jetting	Elastomer-like resins Acrylic-like resins Epoxy and Polyurethane	Bellows Membranes Octopus-like tentacle shapes	Pneumatic Shape memory wire

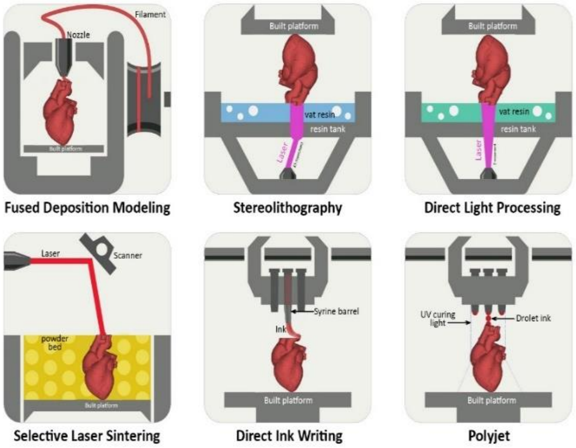

Fig 1. The commonly used 3D printing processes are shown schematically below: Fused Deposition Modeling (FDM), Stereolithography (SLA), Digital Light Processing (DLP), Selective Laser Sintering (SLS/SLM), Direct Ink Writing (DIW), and Material Jetting (MJ/Polyjet). [20]

2.2. Material and fabrication process

We are comparing two different ways of making unique materials. One way is by creating multi-walled carbon nanotube (MWNT) graphene-based electrodes. The other way is the traditional method of making ionic polymer-metal composite (IPMC) actuators [28]. Using polyjet printing methods to make a particular device that can move using liquids and is made from different materials [29]. Polyjet printing and single-material digital light projection (DLP) are examples of printing actuators using ultraviolet (UV) resins [30]. There are two ways to make graphene nanoribbons: top-down and bottom-up approaches. In the top-down approach, you start with a big graphene sheet and then shape it into the small nanoribbons you want. On the other hand, the bottom-up approach involves putting together tiny building blocks to form the larger nanoribbons you desire [31]. A graphene-based epoxy composite is produced using a casting mold, and the epoxy material is acquired with the graphene to achieve the epoxy composites [32]. The fabrication of graphene using graphene-based composites or high-temperature chemical vapor deposition results in organic photovoltaic cells (OPVs). Employing a spin coating of graphene solution demonstrates polymers in organic photovoltaic cells (OPVs); the electron donor is poly-(3-hexylthiophene) (P3HT), and the acceptor is phenyl-C61-butyric acid methyl ester (PCBM) [33]. The composite filament for 3D printing was fabricated through the following process: Initially, thread-like PLA was pulverized using a pulverizer. Next, the pulverized PLA was combined with the second thermally reduced graphene (t-r-GO) and introduced into the HAAKE twin-screw melt mixer. At 160°C for 15 minutes, the mixing was carried out with the rotating screw at a speed of 80 r/min. Before cooling, the composite is cut into pieces and pulverized into powder. To form filaments from this powder, the authors employed a mini screw extruder with a diameter of 1.75 mm [34]. Energy dosage characterizations of the pre-polymer mixtures were performed utilizing the drawing of circles to manufacture them for use in the stereolithography apparatus (SLA). [35]

2.2.1. Smart materials graphene based

Graphene-based actuators often have bilayer-multilayer structures or unimorph just one-layer configurations. A graphene layer with different compositions on each surface is the basis for the standard unimorph graphene actuator [36]. Pure polymers and polymer composites have recently been used as light-triggered polymeric actuators [37-38]. Two actuator materials must have "molecular switch" and "energy transfer" units in the intermolecular stages. The former acts as a trigger (energy transfer) unit to transfer outside light energy to the "molecular switch" unit, and the latter acts as a mechanical deformation (molecular switch) unit [39]. Its most developed 3D printing method is SLA. Layer by layer, flowing ink is printed in SLA. The surface is simultaneously laser-irradiated to harden the desired area. This process is continued until the desired product is obtained [40]. A multi-material structure is often used to make ion-responsive hydrogel actuators. This structure has neutral, non-ion-responsive gel layers and an ion-responsive gel (polyelectrolyte). As an illustration, Wong and colleagues created neutral poly (ethylene glycol) diacrylate bi-material hydrogel actuators using SLA in the form of anionic poly (acrylic acid) [41]. The mechanical characteristics of the components produced by SLA and 3D printing depend on the level of cross-linking attained. It follows that the effectiveness of the chosen photoinitiators will have a significant impact on these characteristics. It is crucial to remember that aqueous solutions are the ideal method for producing hydrogels when printing them using SLA. [42]

2.3.Ionic based hydrogels actuation

Interconnected polymeric chains held together by tie points or joints make up the intricate three-dimensional hydrogels. Covalent bonds, ionic bonds, hydrogen bonds, physical entanglements, or dipolar interactions have these joints together [43]. A typical ionic polymeric actuator system consists of two counter electrodes and an elastomeric electrolyte with various-sized cations and anions [44]. In ionic polymer-metal composites (IPMCs) actuators, metal composite electrodes are linked to both sides of the polymer to create an electric field and prevent the water from drying out [45]. Ionic polymers that contain water are employed as the functional layer [46]. Researchers have developed ionic polymer-metal composites (IPMCs) actuators to address the shortcomings of hydrogel actuators (i.e., electrolyte environment and operating voltage) using a multi-walled carbon nanotube (MWNT)-graphene-based electrodes and conjugated polymers, such as polypyrrole (PPy) and polyaniline (PANI) [47]. The electroosmotic water flow between two electrodes (from anode to cathode) in an electric field is how hydrogel actuators, like IPMC actuators, work [48]. Through the innovative technique of 3D printing, hydrogel materials can be transformed into objects that exhibit controllable actuation, and this technology enables the realization of intricate hydrogel designs, facilitating access to complex programmed actuation. The manufacture of custom-shaped IPMCs via 3D printing entails four main phases. Fused-flame 3D printing for IPMCs includes the following steps: printing a soft structure using an ionomeric material precursor, functionalizing the printed precursor structure, plating the printed design, and dividing and wiring electrodes for multi-DOF actuation. [49]

3. Bioinspired smart actuator

Some soft smart actuators based on unique phenomena of living organisms, animals, and humanity have an intelligent response to interplay with environmental stimuli, known as bioinspired smart actuators. Creating soft, moist anisotropic actuators based on hydrogels with color-changing capabilities is similar to the intriguing traits in some natural animals like chameleons and flowers. These biologically inspired actuators have enormous promise in various applications, such as soft robotics, synthetic muscles, biosensors, intelligent bionics, and smart valves. pH-responsive perylene bisimide (PBI)-functionalized with fluorescent hydrogel components can be "switched on" or "switched off" in response to changes in the surrounding pH environment thanks to the thermoresponsive properties of graphene oxide (GO) and poly(N-isopropyl acrylamide) in the hydrogel layer [50]. Graphene oxide (GO) has been widely used as a physical cross-linker to create stimuli-responsive hydrogels in conjunction with other cross-linkers to create humidity-driven graphene-based smart soft actuators [51]. The asymmetric GO/RGO structure would cause unsymmetrical deformation in humidity and automatically alter the shape because water adsorption might cause apparent expansion due to differing absorption capacities in Fig 2. [52].

3.1. Finite element modeling

Simulating soft structures, actuators, and sensors is challenging because of their considerable nonlinearities in such soft robotic systems. Because it accounts for the geometric nonlinearities caused by significant mechanical deformations, the material nonlinearities caused by the inherent nonlinear behavior of the materials used in such systems (i.e., stress-strain behavior), and the contact nonlinearities caused by the surfaces that come into contact during deformation, finite element modeling (FEM) is successful in representing soft and deformable robotic systems [53]. For the first time, experts have used a unique method to study how a 3D-printed object's structure works. Javad Zarbakhsh et al. [54] combined techniques and tools, like nesting sub-models and Finite Element Analysis. This helped them understand how the different parts of the printed object behave. The authors even looked at the specific patterns created during the 3D printing process. This is a new way to learn how 3D-printed things hold under pressure. FEM can be used to optimize the performance and topology of such soft robotic systems to satisfy specific design and performance requirements. This is done before the manufacture of the soft robotic systems. Finite Element Modeling (FEM) is a flexible computer simulation method for structural and multi-physical investigations [55]. Identifying the abstraction level and model complexity are two issues in FEM simulation. Embedded Elements (EE), a particular finite element technique included in commercial FEM software like Abaqus, Ansys, nTopology, and others, might provide a different and practical approach. The reinforcing fibers can be modeled using this method apart from the matrix surrounding them, and it can be applied to three-dimensional fiber patterns rather than flat. Finite-element modeling and analysis were done to simulate the loading test of the wall and examine the behavior of the 3D-printed wall construction in the loading tests using the elastic-modulus and compressive strength data from the previous section. The FE diagram for a single simulation of a soft pneumatic actuator or sensor is shown in Fig 3. It shows each phase in detail. The "Static Structural Analysis" in ANSYS Workbench (ANSYS Inc.) was used to execute the FE simulations. The soft actuators and sensors' 3D CAD models (i.e., geometries) were instantly imported into ANSYS "Design Modeler" [56]. The orientation of the filaments and the presence of an air gap in fused filament fabrication (FFF) materials are expected to result in high anisotropy.

Consequently, a thorough understanding of the regional phenomena that emerge while loading the material will be necessary to simulate their behavior [57]. Finite Elements to forecast the mechanical performance and comprehend the failure mechanism of 3D-printed composite, a model of the material is developed using the representative volume element (RVE) method. The mechanical properties of 3D-printed composites comprised of diamond abrasives and aluminum alloy binders are mimicked by Digimat-FE and Digimat-MF modules. FEM can be used to improve the performance and topology of soft pneumatic actuators and sensors that can be directly 3D printed using open-source and affordable FDM 3D printers. FEM accurately predicts their behavior and performance. FEM can successfully handle the nonlinearities needed in modeling soft robotic actuators and sensors, which are essential parts of soft robotic systems; as a result, saving a tremendous amount of time and money [58].

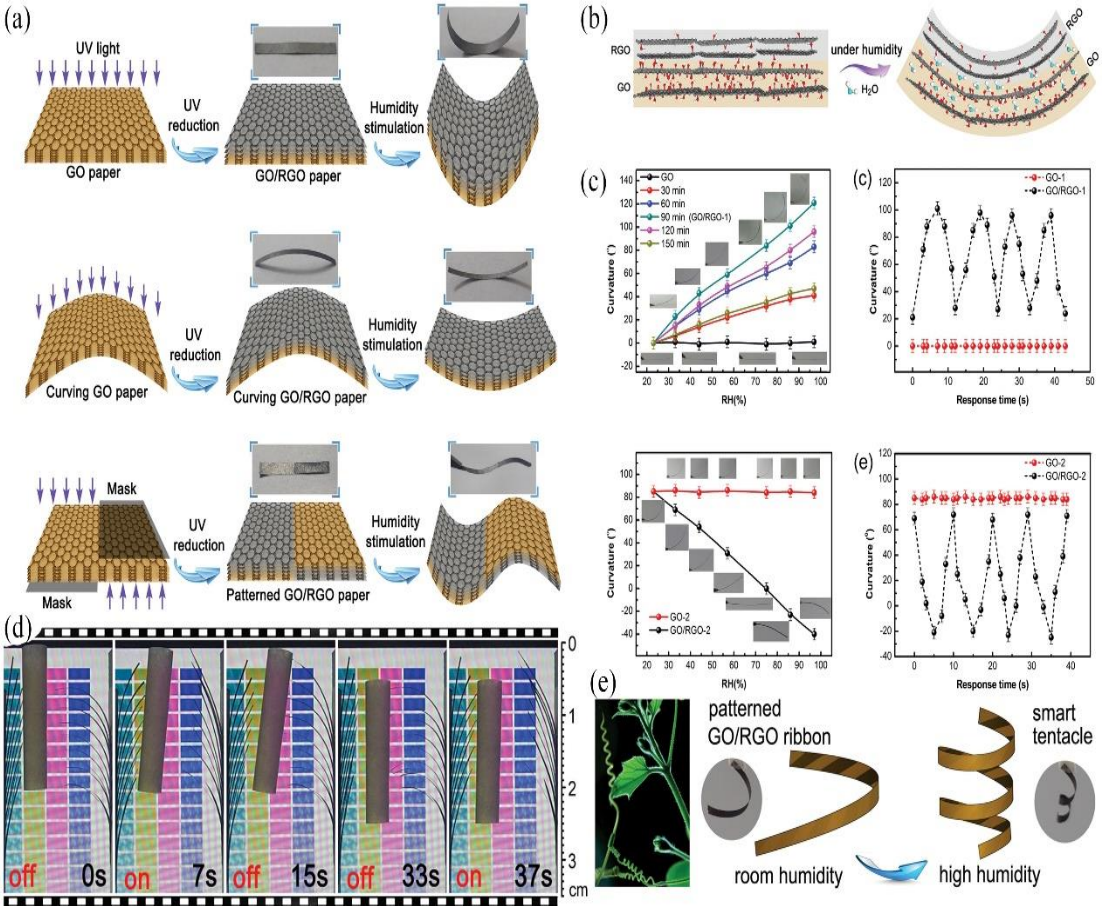

Fig 2. Schematic representation of the (a) GO/RGO bilayer actuator design principle shows the predicted responsive behaviors of the flat GO/RGO paper, the curved GO/RGO paper, and the patterned GO/RGO paper in humidity, (b) the method in which the GO/RGO bilayer structure bends. For ease of identification, oxygen atoms in water have been shown in distinct colors, (c) GO paper and various GO/RGO bilayer sheets' bending angle curves, a comparison between the reversible response of the GO/RGO-1 sample and GO, (d) Smart graphene "cilia" created by GO/RGO-1 and GO/RGO-2 ribbon arrays are shown on the left and right, respectively. A paper cylindrical shell could be swept using the intelligent cilia. The terms "on" and "off" refer, respectively, to turning on and off the humidity, and (e) patterned GO/RGO ribbon with diagonal stripes was created by UV irradiation with the aid of a mask; of smart graphene "tendril" inspired by tendril climber plant. [52]

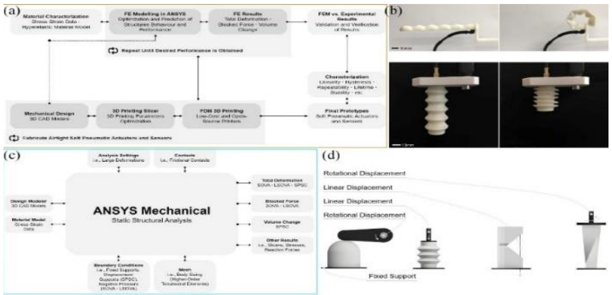

Fig 3. (a) The technique of creating airtight, optimal soft 3D printable pneumatic actuators and sensors through modeling and fabrication, (b) Soft vacuum actuators (SOVA) are bendable and linear soft vacuum actuators (LSOVA) actuator's starting position- a single SOVA actuator at its beginning position when no vacuum is supplied, and in its final position when (90%) vacuum is applied, (c) Diagram for pneumatic soft actuators and sensors using finite elements simulations, and (d) Soft pneumatic sensing chambers (SPSCs) that are perceptive to compression, bending, torsion, and rectilinear displacement in addition to the other four basic mechanical input modalities. [53]

3.2. Soft actuator mechanism

The force transfer required by robotic mechanisms is frequently prevented by soft materials alone; energy physically deforms the soft mechanism rather than being transported to or from the environment. Microrobots can endure significant deformations when printed using soft materials like multi-walled carbon nanotube (MWNT)-graphene. Modeling the ensuing processes can also be made more accessible by rigid links separated by soft flexures [59]. Light-responsive actuators frequently employ intermediary energy-conversion techniques to accomplish the goal of mechanical deformation eventually. The actuating mechanism is split into three categories based on the intermediate energy conversion: photo-thermal, photochemical, and photo-electric conversion actuation [60], among the three actuation mechanisms mentioned below in Fig 4. The most popular actuation techniques are photo-thermal and photochemical, particularly when combining sophisticated light-responsive nanomaterials with polymers. Three types of photo-thermal transformation actuation exist, as well as photo-thermal phase transition deformation, these processes also involve photo-thermal expansion deformation [61]. A typical design strategy for photo-thermal expansion actuators is the bilayer construction. Photochemical materials respond to light by going through a chemical change similar to a crystalline transition, which typically causes a change in geometry [62]. Azo-benzene and spirogyras, two photochemical chemicals that have seen increased application recently, are frequently combined with liquid crystal materials or hydrogels, especially azo-benzene. This is mainly caused by the photo-deformation of liquid crystals with azo bases responding to light more quickly [63]. When exposed to a particular light wavelength, nano/micron carbon materials go through a transition that promotes the amplified vibration of the carbon nanolattice to produce heat and can be optically activated by light and magnetism [64]. For instance, the light-actuating potential of a unique 3D-linked graphene sponge was studied. [65]

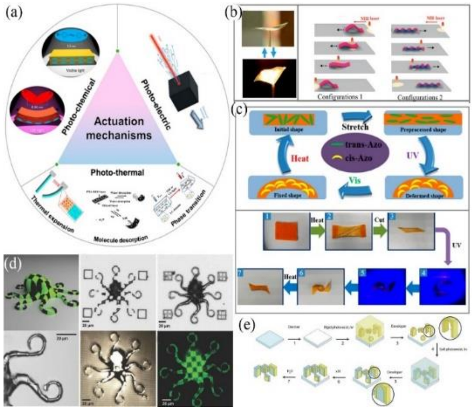

Fig 4. (a) A diagram of how the bilayer structure of a PDA-RGO/NOA-63 actuator bends and straightens in response to changes in humidity (top panel) and periodic NIR irradiation (bottom panel). Photo-thermal effect of GO film and the thermally induced phase transition of LC domains upon NIR or Vis irradiation the photo-electric conversion mechanism Transformation of trans/cis isomeric azo-benzene, (b) Actuating behavior of LCP film when heated by IR lamp. Schematic of the approach to optically reconfiguring an LCN actuator through selective de-crosslinking, (c) Mechanism in molecular Structure; Experimental Deformation numerous light-responsive liquid crystal elastomer materials have also been created based on this phenomena, [60] (d) Microscale of two materials 3D printing using two photon polymerization, a concept drawing of an octopus made from two different materials, and view of the hybrid urethane diacrylate UDA/IP-DIP tentacles in a higher resolution, and (e) Scheme of the multimaterial fabrication. [59]

4. Multi responsive soft actuators

There is growing interest in developing soft actuators that can adapt to various inputs and configurations. Thermodynamic equilibrium is reached when hydrogels, three-dimensional network structures of polymeric chains connected by tie points or joints, swell in water. Developing actuator-based soft robotics and biosensors is exciting in hydrogels that can react to electrical stimulation, pH, and temperature. Due to their considerable potential for biological and medical applications, responsive polymers that react to thermal, chemical, pH, UV, electrical, magnetic, and other stimuli have received a lot of interest in recent years. Hydrogel conducting polymers and their mixes are among the many that can exhibit this kind of activity and are frequently studied.

4.1. Chemically responsive (pH, UV, Moisture etc.)

Flexible polymer actuators have garnered significant interest recently due to their wide-ranging applications. Researchers have focused on creating diverse stimuli-responsive polymeric systems. These systems exhibit shape-shifting properties when subjected to light, electricity, magnetic fields, humidity, pH variations, or temperature changes. A notable example is the development of a pH-responsive anisotropic microporous composite actuator using polypropylene (PP) and liquid crystalline network (LCN) materials. This hybrid bilayer actuator can be deliberately set into a specific shape and locked in place, allowing for precise and programmed actuation capabilities (Fig 5a,5b) [66]. Graphene and carbon nanotubes have emerged as promising materials for actuator applications owing to their exceptional light absorption, flexibility, and efficient thermal conductivity. Light-responsive polymers have garnered significant interest in science and engineering due to their unique benefits. Hydrogels, shape-memory polymers, and liquid-crystalline elastomers (LCEs) are notable examples in this category. A particularly intriguing avenue involves the integration of photochromic molecules like azobenzenes into polymer networks, which facilitates the creation of light-responsive LCEs with remarkable properties [67-68]. The responsiveness of LCN actuators is programmable because the alignment patterns of LC (Liquid Crystal), the distribution of photo-cross-linking regions, and the use of strategically placed external stimuli are all done on purpose. These actuators are composed of liquid crystal networks doped with azobenzene (MAB), collectively referred to as ALCN, and incorporate graphene oxide (GO), resulting in what is known as a GO-ALCN actuator. Remarkably, the bilayer film of GOALCN exhibits exceptional photothermal propulsive capabilities, opening avenues for the creation of an array of intelligent devices and robots. This advanced actuator can emulate the intricate blooming and closing movements akin to flowers triggered by UV or NIR light sources [69]. The pliable substances, characterized by their unique affinity for water molecules, have found extensive application in crafting biomimetic moisture-responsive actuators in Fig 5c-e. GO, a derivative of graphene containing numerous hydrophilic oxygen-containing groups (OCGs), has emerged as an up-and-coming contender for moisture-responsive actuators. Over the past half-decade, GO-based moisture-responsive actuators have exhibited distinct merits compared to alternative materials and devices in their responsiveness to various stimuli. GO's hydroxyl, epoxy, and carboxyl groups on its sheets can establish hydrogen bonds with water molecules through robust interaction. As a result, GO exhibits remarkable water adsorption abilities when exposed to moisture, which causes a noticeable swelling effect. [70]

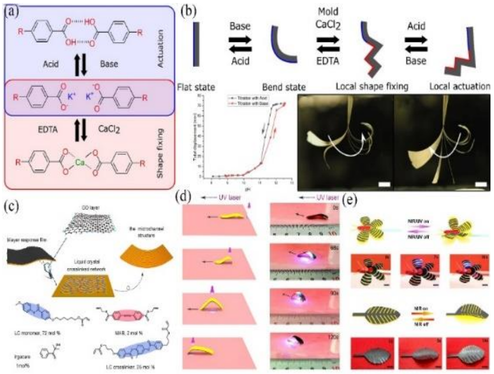

Fig 5. (a) Molecular mechanism for fixing and pH-responsive actuation, (b) a schematic of the pH-responsive LCN region is shown in blue, the LCN shape-fixed portions are shown in red, and the PP scaffold of the composite film, a actuator's displacement titration curve with a cut perpendicular to the fibrils, [66] (c) Schematic representation of the interior microstructure and material composition of the azobenzene doped liquid crystal network (ALCN) bilayer membrane, (d) Crawling robot with an inside layer of GO and an outside layer of ALCN film that reacts to UV light, and (e) Real-time photos of biomimetic deformations of the artificial leaf in response to NIR light. Demonstration of biomimetic behaviors of GOALCN microrobots with a patterned GO layer. [69]

4.2. Electrically responsive

Electrically responsive soft actuators play a significant role in designing and constructing ground-breaking soft robots and devices. However, surprisingly few alternatives for soft materials are 3D-printable and electrically responsive [71]. The actuator comprises two 3D-printed segments: an active chain and a passive chain. It is a parallel electroresponsive mechanism. The active chain comprises two electrically responsive hydrogel actuator links and is connected to the ground at one end shown in Figs 6a-b. On the other hand, the passive chain consists of two hard polymer links connected to the active chain at one end. A 3D bio-plotter that uses extrusion and polyelectrolyte hydrogel as the printing ink is used to print the actuator links [72]. It is possible for many different short peptide types to self-assemble into the entangled fibrous network architectures of hydrogels. The hydrogelator we employed to create the supramolecular hydrogel network was a short peptide. The hydrogelator's self-assembling motif was 2-naphthalenyl-glycinephenylalanine-phenylalanine (NapGFF). By our lab and others, this motif has been thoroughly investigated for the creation of peptide hydrogels [73]. These gel systems can transform electromagnetic energy into mechanical energy, simulating how living things move when exposed to external electromagnetic stimuli. However, low-responsive efficiency and restrictions of the liquid electrolyte environment are downsides [74]. Ionogel electrolytes can be made with several desirable characteristics for electrochemical actuators, including direct low-voltage control in the air, good electrochemical and thermal stability, and complete silence during actuation [75]. Self-initiated UV polymerization produced essential nanocomposite gel electrolytes from HEMA, BMIMBF4, and TiO_2 via a cross-linked supramolecular approach. Robust and stable ionogels that mimic electric double-layer capacitors are emerging to enable soft actuators powered by electrically induced ion migration. In Fig 6c below, the google-based actuator displays a displacement response. [43]

4.3. Thermally responsive

Numerous scientific principles involving phenomena such as the shift from liquid to vapor states, the captivating phenomenon of shape memory, and the notable bilayer composite effect have been extensively utilized in the field of flexible materials like Ecoflex, liquid-crystalline elastomers, and polylactic acid (PLA). These various mechanisms have gained significant attention for fabricating pliable actuators with temperature-sensitive properties that can quickly return to their original conditions. The appeal of these actuators stems not only from their functional capabilities but also their lightweight characteristic [77]. However, thermal-responsive hydrogels are challenging to fabricate by crosslinking into smart devices due to their poor mechanical properties [78]. Hydrogel has a significant water content with a three-dimensional polymer network. To prepare hydrogel-based thermo-responsive soft actuator crosslink done by coupling reaction hydrogel with graphene oxide (GO) or hydrogel with hydrolyzed vinyltriethoxysilane (VTES). Therefore, significant efforts have been made to develop responsive hydrogels with improved strength and toughness. Graphene and its derivative, graphene oxide (GO), have been harnessed to strengthen and enhance the functionality of polymer hydrogels, capitalizing on their expansive specific surface area, thermal impact, and abundant surface functional groups. As GO nanosheets integrate with monomers, the interplay of hydrogen bonding ensues, fostering connections between monomers or hydrophilic polymer chains and GO and amplifying their strength and toughness. Bilayer composite configurations containing various membranes, including pairings like polylactic acid (PLA) and paper layers, each marked by unique thermal attributes, demonstrate a dependable and repeatable reaction to thermal excitation. When the temperature exceeds the critical glass transition point, the polymer layer experiences a softening transition while being heated, leading to the extension of the flexible actuator. Conversely, during the cooling process, the composites return to their initial pre-defined shape due to the intrinsic recuperative impact of the bilayer phenomenon. In this context, a thermoresponsive hydrogel with anisotropic properties is created through the sequential process of linear remolding applied to a clay-PNIPAm nanocomposite hydrogel with remarkable stretchability, followed by a secondary crosslinking step. This subsequent crosslinking immobilizes the reconFigd polymer network, forming a hydrogel with thermo-responsive characteristics [79]. Gamma-ray irradiation, a novel crosslinking technique devoid of radical initiators, was also used to create the hydrogel-based thermoresponsive actuator for biomedical soft actuator applications. The production of thermo-responsive hydrogel and sterilization can be accomplished using the gamma-ray irradiation technique in a single step without using an additional initiator for the polymerization and crosslinking reactions. As a result, the finished product doesn't need to be further purified and can be used for biomedical purposes. Through the co-polymerization of PNIPAM and PAAm and crosslinking assisted by vinyl-modified GO nanosheets, thermo-responsive hydrogels have been created. By altering the concentration of GO-VTES and adjusting the molar ratio between NIPAM and AAm inside the hydrogel framework, the resultant hydrogels exhibit improved structural and mechanical properties. A thermoresponsive poly(N-isopropyl acrylamide-acrylic acid) (PNIPAAm-PAAc) or poly(N-isopropyl acrylamide) (PNIPAAm) active layer with a passive layer made of poly(acrylamide) (PAAm). The lower critical solution temperature (LCST) for PNIPAAm, a typical temperature-responsive polymer, is 32 ºC in aqueous conditions, where it undergoes a reversible phase shift upon a slight external temperature change. But when the temperature rises over the LCST, the connection between polymer chains takes over and causes the hydrogel to shrink quickly shown in Fig 7. [80]

4.4. Magnetically responsive

Magnetic soft actuators have emerged as promising tools in biomedical applications, especially in the domains of minimally invasive surgery, in vivo imaging, and drug delivery. These soft actuators can execute precise locomotion guided by an external magnet or a programmable magnetic field. Their ability to be controlled remotely via magnetic force has been extensively explored, revealing their capacity to withstand fluid flow when subjected to a magnetic field. Upon removal of the magnet, these miniature soft actuators exhibit controlled forward movement through conduits. Additionally, researchers have successfully developed degradable silk-based soft actuators with magnetic responsiveness through techniques such as thermal forming and plastic molding of magnetic silk films. These fabricated soft actuators can be precisely actuated and directed within solutions using an external magnet [82-83]. This magnetically interactive actuator showcases dependable actuation capabilities with instantaneous field responses. The need for intricate mechanical and electrical control systems is eliminated. A magnetically interacting actuator is envisioned and presented, drawing inspiration from the ciliary structures in living creatures. This design features hierarchical pillars on a film's surface, enabling active, rapid, and dynamic control over the force and velocity applied to a small object through an external magnetic field. Various magnetic pillars with distinct morphologies are produced using a modified soft lithography technique involving ink-based processes and imprinting. Upon exposure to an external magnetic field, these pillars rhythmically flex and restore their shape in a controlled manner. The resultant force can be harnessed to propel or capture a small object effectively [84]. Magnetic Fe_3O_4 nanoparticles have been harnessed in creating a digital light processing 3D printing resin. This unique resin is instrumental in producing versatile soft actuators capable of multi-material printing through a free assembly approach. By employing magnetic and nonmagnetic resins to represent their respective segments, this technology facilitates the fabrication of various magnetic devices and actuators using digital light processing (DLP) 3D printing in Fig 8a,8b [85]. Emerging demand for reprogrammable soft actuators with magneto-responsive capabilities within confined spaces has propelled the development of next-gen smart devices. Leveraging the integration of Liquid Crystalline Elastomers (LCEs) with diverse magneto-responsive thresholds, these actuators enable precise, localized, and sequential magnetic control, adapting seamlessly to evolving conditions (Fig 8c,8d). [86]

4.5.Photo responsive

In addition to their particular advantages of flexibility, contactless operation, and remote control, as well as their numerous technological applications ranging from bionic robotics and biomedical devices to nanomotors, photoresponsive soft actuators with photomechanical energy conversion and flexibility have attracted significant interest in recent years. Researching for effective photoresponsive materials that may be used to create advanced photo actuators that have high energy conversion efficiencies, reliable mechanical properties, and other such qualities (Fig 9a) [87]. In contemporary technologies, such as soft robotics, artificial muscles, and bionic devices, soft materials with high flexibility and the ability to induce huge deformations play essential roles. Thermal-mechanical conversion materials are among photoresponsive actuators' most appealing stimuli-responsive soft materials. Photochemical reactions involving molecular deformation are the basis for photochemical actuators. Numerous photoactive groups, such as azobenzene, anthracene, diarylethene, spiropyran, fulgide, Schiff bases, etc., experience reversible shape-changing photoreactions [88]. Carbon compounds like CNTs, graphene and its derivatives, graphite, and amorphous carbon have been used as effective photo-actuating materials. Finding appropriate photo-actuating materials and straightforward manufacturing techniques to generate high-performance photo actuators is vital for efficiently combining carbon materials with various light actuators and the various actuating schemes discussed [89].

A monolayer graphene oxide (GO) photo actuator was created, as illustrated in Fig 9b, in addition to the gradient component structure. Fused deposition modeling (FDM) is a type of 3D printing method that does not require exposure to UV light, as opposed to 3D photopolymerization printing technology. To prevent the considerable impact of UV irradiation during the 3D printing process, FDM can be used to create photoresponsive devices. 3D printable shape memory devices include photo responsiveness thanks to incorporating carbon black (CB) into PU. Thus, our hypothesis was that shape memory polymers PU and photothermal conversion materials CB may be combined to create photoresponsive shape memory composites PUCB. Layer-by-layer deposition creates 3D printable photoresponsive shape memory devices using the materials in Fig 9c for FDM [90].

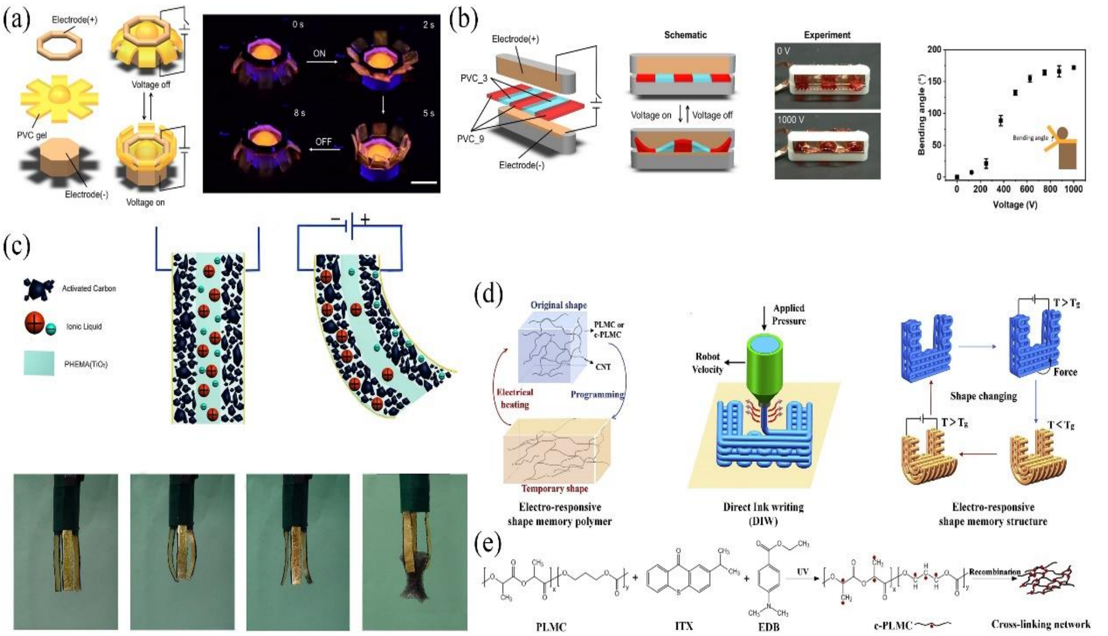

Fig 6. (a) Diagram showing the setup and workings of an "Jellyfish" actuators that were 3D printed, rhodamine B, a fluorescent dye, has been incorporated into the ink to aid with visualization, (b) By printing PVC_3 and PVC_9 onto a single sheet, a gel actuator may be created that a voltage of 1000 V is applied, the actuator produces an undulating motion, [71] (c) Schematic representation of an actuator based on an ion transfer mechanism and made of $BMIMBF_4$ gel electrolyte, [43] and (d) shape memory nanocomposites created by 3D and 4D printing, the printed material's electro-responsive shape memory characteristic, the DIW technique, the 4D-printed structure's electro-responsive shape-changing behavior, and (e) PLMC reacts with UV to cross-link, forming c-PLMC. [76]

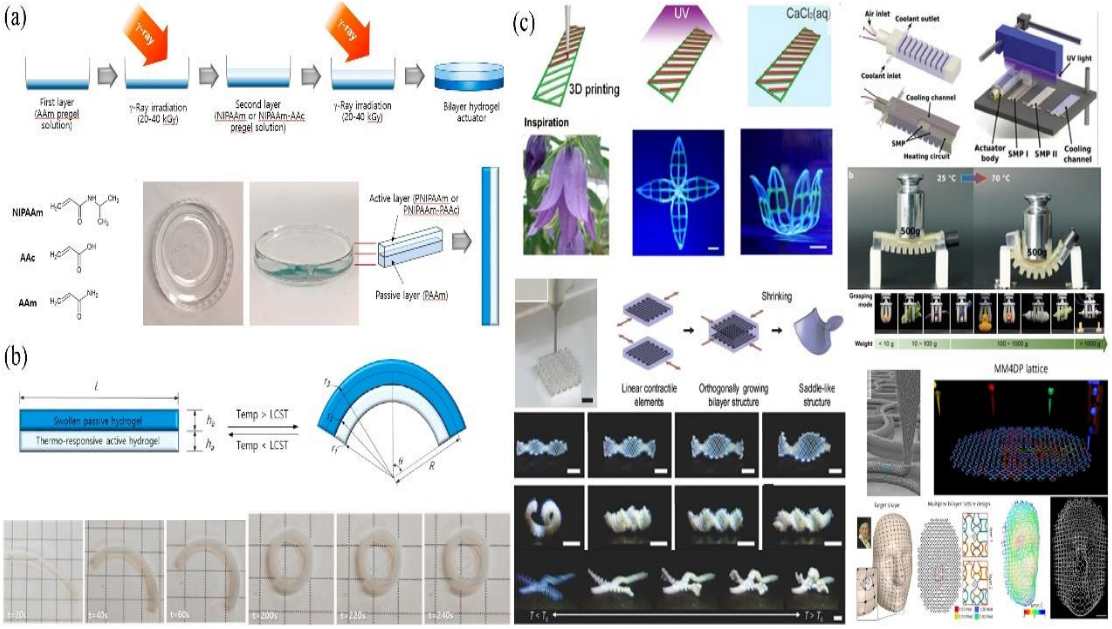

Fig 7. (a) Schematic of the gamma ray radiation is used in the process of creating a bilayer, temperature-responsive hydrogel, the structure of the NIPAAm, AAc, and AAm monomers that were employed to create hydrogels, (b) the mismatched tensile between the swelling and nonswelling layers causes the bilayer hydrogel of a temperature-responsive material to bend, PNIPAAm/PAAm-0-20/20k bending actuation at 50°C, [80] and (c) temperature-responsive intelligent structure made using the DIW technique: Digital inkjet printing of an intelligent structure with temperature sensitivity, robotic gripper DIW printing, reproduction permitted, DIW printing of multimodular 3D structures and essential linear contractile parts, DIW printing of multi material lattice structure. [81]

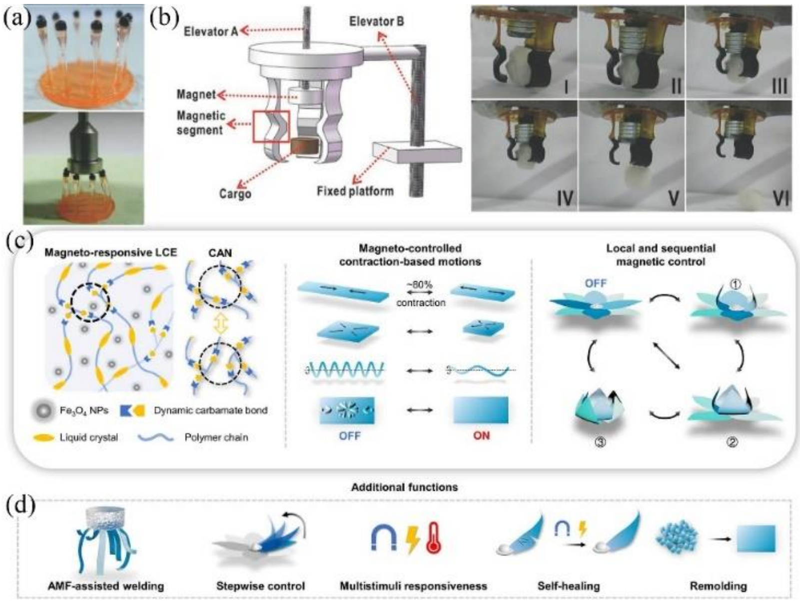

Fig 8. (a) A complex construction that was DLP 3D printed that had several matches, including an isometric perspective view, and a bent shape in the presence of a magnetic field, (b) An illustration of the magnetic driving gripper system in a schematic form, a demonstration of a 3D-printed gripper successfully catching and moving a cotton ball under the control of a magnet, [85] and (c) Diagram of the magnetic LCE actuator with reprogrammable functions. The method of creating reprogrammable magnetic soft actuators with diversiform contraction-based motions by fusing magneto thermal responsiveness with covalent adaptable networks (CAN) in LCEs, and (d) the reprogrammable magnetic actuators with additional advantageous features, such as AMF-assisted welding, stepwise magnetic controllability, multiresponsiveness, self-healing, and remolding capability. [86]

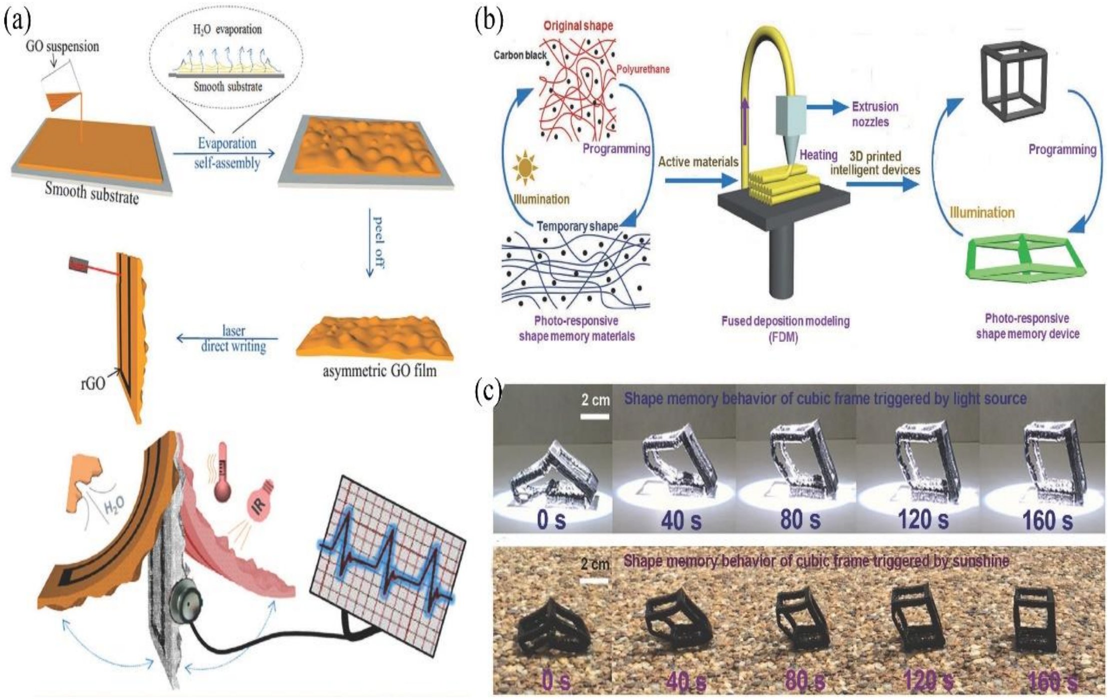

Fig 9. (a) The synthetic path of the GO film photoactuator is depicted schematically- a coating for GO suspension, evaporation of solvents, an irregular surface morphology, derived GO film with asymmetries, the rGO circuit helped by lasers, a sensor-integrated, manufactured multistimuli responsive actuator, [87] (b) Carbon black and polyurethane-based 3D printing materials have photoresponsive shape memory characteristics using fused deposition modeling, to print devices on a glass panel using layer-by-layer deposition, 3D printed device's photoresponsive shape memory behavior, and (c) Cubic frame form recovery under 87 mW cm^{-2} of light source and 76 mW cm^{-2} of sunlight. [90]

4.6.Applications of 3D printed polymer-based gripper

We explore practical uses for soft actuators, including Soft grippers, biomedical devices, object manipulation, and human-machine interfaces (Table 2). Hydrogel grippers are one of the most common applications, typically made of bilayer structures. The idea was illustrated using a bilayer of shape-memory hydrogels made of poly (N, N'-dimethyl acrylamide-co-stearyl acrylate) (P(DMAAm-co-SA)) with varying concentrations of the crystalline monomer SA. The mechanical and swelling anisotropy that led to the actuation movements resulted from varying SA concentrations in the gel. One of the exciting potential applications of 3D-printed hydrogel actuators was the development by the Spinks research team of an intelligent valve based on 3D-printed alginate to control water flow. Recently, a 3D-printable biomimetic ink was developed that enables actuators to change their shape, luminescence, and opacity in response to humidity or (de)hydration. This technique was influenced by how plants and marine life respond to stimuli by changing their shapes or colors (Fig 10). [91]

Table 2. Desired capabilities and features (challenges) relevant to an application [91].

Applications	**Challenge**
Soft grippers	Movement accuracy, gripping accuracy, and environmental conditions (dry, moist, vacuum) adaptation
Artificial muscles	comparable to biological muscles in terms of life cycle, adaptability, energy density, actuation stress, actuation strain, and strain rate.
Sensor-integrated soft robots and wearables	Sensing shape, location, and condition; recognizing external stimuli (such as electromagnetic waves, light, heat, and sound); and flexible conductive lines and electrodes.
Haptic displays	Sensing bulk qualities, such as elasticity, hardness, and elongation; and sensing surface properties, such as roughness, friction, softness, and viscoelasticity.
Biomedical devices	Devices for surgery and rehabilitation: conformability, adaptability, and safe contact Soft milli- and microrobots: biocompatibility, controlled actuation, localization, navigation in challenging three-dimensional environments.

Biomedical devices and drug delivery systems must operate safely in vivo. Therefore, once they reach the desired regions, soft surgical robots should be highly skilled and effectively transmit force. They must also be flexible and stiff enough to resist fluid flow and overcome barriers while navigating difficult in vivo situations. Magnetic catheters may be guided in tight, constrained 3D environments thanks to contactless, high degrees-of-freedom magnetic navigation. A micro-catheter with a magnetic head and flow-driven navigation can move automatically through blood arteries and be magnetically guided at the bifurcation position**.** The most minor section of the micro-catheter has a diameter of 25 µm. This approach offers the best chance of navigating in small, branching vessels since it requires less human intervention and poses a lower danger of iatrogenic injury. Stretchable sensors that have been turned on contour to the surface of the heart, potentially enabling the creation of an entirely soft and conformal electrophysiological device for sensing and therapeutic uses. A catheter can be used to deploy a balloon actuator that has been integrated with a flexible sensor array. Since they may be magnetically directed and affixed to a tumor, capsule endoscopes can also perform under-tissue biopsies using a fine-needle biopsy tool. [92]

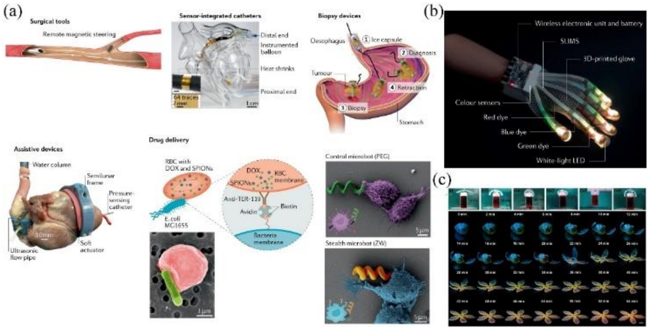

Fig 10. (a) Soft actuators in biomedical applications include wireless blood vessel navigation using a functionalized catheter, balloon catheters with conformal electronics, small biopsy devices that can deliver drugs through biohybrid soft actuators, and artificial soft actuators that can evade macrophage detection, [91] (b) modern soft actuators that could be used in industries With the use of a wireless, soft wearable glove, a high-resolution soft sensor with optical

output made of elastomeric light guides was demonstrated, and (c) A 3D macro gripper in various bending positions, Four-dimensional printing of simultaneous full-color luminescence tweaking and form morphing structures. [92]

Customized objects with complicated geometry can be produced quickly and affordably with 3D printing. Many materials, including polymers and composites, are available, each with unique qualities (strength, stiffness, chemical resistance, etc.). With these benefits, 3D printing satisfies the requirements for robotics applications as they stand now. Because of the limitations of current manufacturing techniques, conventional robotics must be assembled from many different parts, which takes a lot of time. By doing away with specialized molds and labor-intensive assembly processes, 3D printing offers solutions to engineering difficulties in manufacturing robots. Engineers are actively adopting 3D printing for robotics in the industry. One illustration is the production of robot grippers, which is expensive and necessitates extensive customization for various purposes. Printing these parts allows the components to have a lightweight, compact design, unlike typical heavy, non-customized designs, resulting in more excellent performance, such as faster movement and higher load. For instance, Haddington Dynamics uses 3D printers to create robot arms, including a gripper for GoogleX and NASA. Soft robots have drawn much attention because they can carry out intricate actions under challenging or unpredictable conditions. The creation of soft robots, inspired mainly by biology and improved over millions of years, is made possible by advances in 3D printing technology and functional soft materials. As seen in Fig 11a, a frog robot that can jump utilizing combustion power was created using the MJ 3D printing method. Another illustration of cutting-edge 3D printing is the octobot, a robot that resembles an octopus. The essential parts and schematic of an octobot are shown in Fig 11b. While molding PDMS gave the octobot its shape, integrated 3D printing technology created the pneumatic networks. It used a high switching frequency for multi-material printing, as mentioned in "ME". The flexible and firm silicone used to make the printed walker represented, as seen in Fig 11c, the muscles and the legs, respectively. When the soft silicone muscle buckles, pneumatic actuators move the stiff leg of the robot laterally and vertically. The frequency of the actuators determines the robot's speed.

Materials having high specific strengths—high strength but lightweight—are required by the machining, structural engineering, transportation, and aerospace industries. Increased stiffness and strength in light materials can be achieved through topological design and optimization of building materials. Usually stretching-dominated, they distort when compressed or pushed in a single direction. The creation of defect-free carbon using two-photon lithography and pyrolysis led to the development of a novel class of plate nanolattices with a theoretical limit on stiffness and strength. [93]

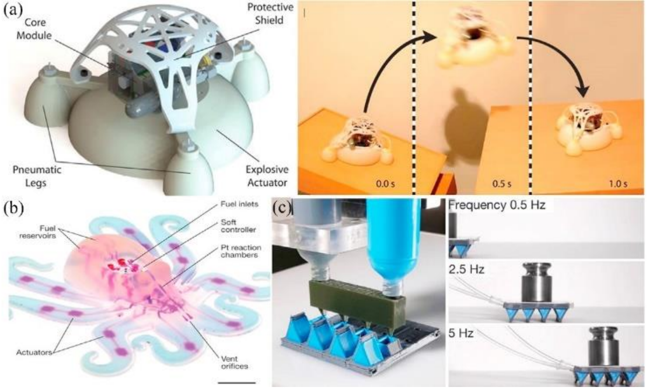

Fig 11. Developed using 3D printing for robotics applications (a) Robot using three pneumatic legs related to a pyrotechnic actuator, (b) Images of a totally soft, autonomous robot (octobot), driven by monopropellant decomposition and controlled by an embedded microfluidic soft controller, and (c) diagram showing the motion of a soft robotic millipede walker. The walker is made of stiff silicone for the displacement caused by an advanced DIW technology (MM3D printing) and flexible silicone serving as muscles. [93]

5.Conclusion and outlook

Flexible nanomaterial sensors are essential for virtual reality applications to deliver a more immersive experience. It can record the user's gestures, posture, and movement. Future advancements in virtual reality sensing could result in higher accuracy and lower latency, combining more sophisticated technologies like machine learning and deep learning. This would enhance user experience and the naturalness of interactions. Smaller and lighter: smaller, lighter, and more easily worn by consumers, enhancing the wearability of virtual reality and facilitating more enjoyable immersive experiences; more types of sensors increase the number of sensors you use, including those for breathing, emotion, scent, and brain waves, to create more sophisticated physiological health monitoring and computer-human interactions. More examples of applications expanded uses in medicine, industry, and education to boost productivity and lower hazards. Strengthen privacy and data security measures to guard against user information misuse or disclosure.

At present, although laser processing of graphene has shown unique advantages in the development of a series of sensors and actuators, there are still many problems that need to be solved for industrial production. First of all, it isn't easy to guarantee the consistency of graphene materials. For example, when graphene oxide is used as raw material, its sheet size, oxygen atom content, and distribution, number of defects are related to the graphite raw material, oxidation degree, and preparation method. In addition, another factor limiting the application of 4D printing of graphene is the relatively low laser processing efficiency. However, efficiency will be significantly improved with the improvement of 3D printing light source quality, advancement of laser processing systems, and development of 3D printing methods.

For successful deep integration of additive manufacturing technology and intelligent materials, research on 4D printing necessitates comprehensive integration of professional knowledge from materials science, information science, mechanical engineering, mechanics, and others. The ultimate objective of 4D printing technology is to directly create structures with specific intelligent functions, which will simplify the complexity of the structure and reduce its weight, which is crucial to enhancing its intelligence. Soft robotics, aerospace, biomedicine, and food development have demonstrated strong application promise for 4D printing technology. The above application domains will see increased use of 4D printing technology as science and technology develop and study is conducted at greater depth.

Based on intelligent health monitoring, clothing will obtain accurate data and realize intelligent, significant, data-assisted judgment. Its non-contact method can help medical staff and community workers remotely monitor the user's physical condition. In the future, health monitoring clothing will be more multi-functional and intelligent and can be widely used in home medical care, sports enthusiasts, elderly care, and other fields. Overall, the future development of virtual reality sensing will make the experience more authentic, immersive, and natural, providing users with a real living environment and working atmosphere experience.

In conclusion, the study of graphene-based polymer intelligent materials and actuators in the context of 3D printing is a ground-breaking combination of innovative technology. The present study highlights the critical function of graphene in enhancing the mechanical, electrical, and thermal characteristics of polymers, hence advancing the development of intelligent materials. 3D printing's accuracy allows for the creation of complex structures with improved functionality, opening up new possibilities for industries like robotics, aircraft, and healthcare. Adding graphene to printed structures not only gives them more mechanical strength but also adds intelligence, enabling behavior that is sensitive and adaptable. The resultant materials are remarkably versatile, having the ability to function as actuators, sensors, and even self-healing parts. This combination of graphene-based compounds and polymer matrices shows promise for revolutionizing manufacturing processes by making them more sustainable, effective, and customized to specific application needs. The study's conclusions guide us as we explore the frontiers of additive manufacturing and materials science and show the way toward the development of novel technologies. A new era of multifunctional materials is being ushered in by the union of polymer intelligence with graphene-enabled actuators in 3D printing. These breakthroughs have the potential to address complicated challenges in a variety of industries.

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Declaration of Competing Interest

The authors declare that they have no known financial or interpersonal conflicts that would have appeared to impact the research presented in this study.

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