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Stimuli-responsive functional materials for soft robotics

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Functional materials have spurred the advancement of soft robotics with the potential to perform safe interactions and adaptative functions in unstructured environments. The responses of functional materials under external stimuli lend themselves to programmable actuation and sensing, opening up new possibilities of robot design with built-in mechanical intelligence and unlocking new applications. Here, we review the development of stimuli-responsive functional materials particularly used for soft robotic systems. This review covers five representative types of soft stimuli-responsive functional materials, namely (i) dielectric elastomers, (ii) hydrogels, (iii) shape memory polymers, (iv) liquid crystal elastomers, and (v) magnetic materials, with focuses on their inherent material properties, working mechanisms, and design strategies for actuation and sensing. We also highlight the state-of-the-art applications of soft stimuli-responsive functional materials in locomotion robots, grippers and sensors. Finally, we summarize the current challenges and map out future trends for engineering next-generation functional materials for soft robotics.

1. Introduction

Soft robotic systems generally refer to robots/devices that are capable of undergoing large deformations due to the inherent physical and chemical properties of the functional materials used to make them.[1–3] This emerging field holds great promise for applications such as artificial muscles, navigation and manipulation, wearable electronics and healthcare. Compared to their traditional rigid counterparts, soft robotic systems feature a high degree of deformability offered by the inherent

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soft materials. Stimuli-responsive materials have been increasingly used to construct soft robots and develop robotic systems with built-in mechanical intelligence.[4,5]

Soft robots and devices can perform desired interactions or tasks in unstructured environments owing to their intrinsic flexibility, stretchability and conformability.[1] External stimuli such as heat, light, electric fields, and magnetic fields can be selectively used to trigger large deformations like isotropic/anisotropic swelling and variation of stiffness.[4,5] However, there are a few challenges in using responsive materials for soft robotics and it requires further design of new stimuli-responsive materials for optimized application of soft robotic systems. A number of existing reviews have summarized the technologies of soft robotic systems or reviewed a specific type of responsive materials in the field of soft robotics.[3,5–7] In this review, we will discuss the fundamental concepts of and the state-of-the-art progress on selection and modifications of soft functional materials toward specific soft robotic applications.

This review is centered on five categories of stimuli-responsive materials widely used for soft robotics, as shown in Fig. 1. Dielectric elastomers (DEs) are the most widely used electroactive polymers (EAPs), which can generate large strain through the Maxwell stress induced by electric activation.[8] Shape memory polymers (SMPs)[6] and liquid crystal elastomers (LCEs)[9] offer reversible, programmable deformations and actuation outputs triggered by external stimuli (mostly heat or light) through vitrification/crystallization of switching domains and reconfiguration of liquid crystal mesogens, respectively. Hydrogels with high water content can withstand large volume change and exhibit excellent biocompatibility, transparency and ionic conductivity.[7] Magnetic materials present a mechanical response to predesigned magnetic fields, which can provide remote manipulation and locomotion guidance for soft robots in confined workspaces.[10] Each material type possesses its advantages and limitations, which play a key role in the performances of the constructed soft robotic systems. For instance, DEs require a high voltage supply and thus one common concern is about electrical safety.[8] SMPs suffer from long transition times owing to the cooling process,[11] and the miniaturization and long-lived deformation of LCEs are challenging.[12] Hydrogels are susceptible to dehydration in dry environments,[13] whereas the biocompatibility of magnetic materials is undesirable due to possible corrosion.[10] Over the recent few years, a wide variety of soft robots and devices have been developed based on the above-mentioned stimuli-responsive materials. For example, soft robotic systems that encompass locomotion robots, grippers and sensors have been demonstrated.[11,14,15]

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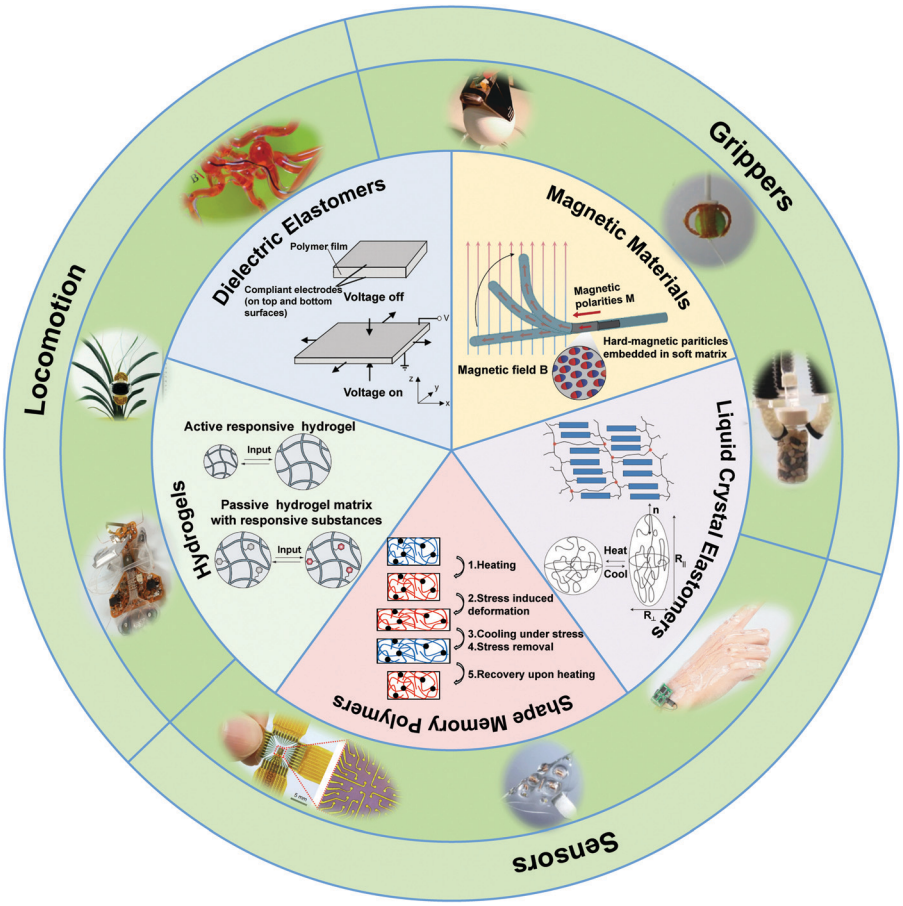

Fig. 1 Overview of typical stimuli-responsive materials and their applications for soft robotics. Dielectric elastomers: reproduced with permission.[16] Copyright 2000, AAAS. Hydrogels: reproduced with permission.[7] Copyright 2020, Elsevier. Shape memory polymers: reproduced with permission.[79] Copyright 2011, Elsevier. Liquid crystal elastomers: reproduced with permission.[9] Copyright 2015, Springer Nature. Magnetic materials: reproduced with permission.[10] Copyright 2019, AAAS. Locomotion (clockwise): reproduced with permission.[121] Copyright 2019, AAAS. Reproduced with permission.[120] Copyright 2018, AAAS. Reproduced with permission.[10] Copyright 2019, AAAS. Grippers (clockwise): reproduced with permission.[141] Copyright 2016, Wiley. Reproduced with permission.[145] Copyright 2018, Wiley. Reproduced with permission.[144] Copyright 2019, AAAS. Sensors (clockwise): reproduced with permission.[70] Copyright 2019, Mary Ann Liebert, Inc. Reproduced with permission.[157] Copyright 2018, AAAS. Reproduced with permission.[156] Copyright 2020, Springer Nature.

This review aims to provide an overview of the stimuli-responsive materials applied in soft robotics. We first introduce the fundamentals of representative stimuli-responsive materials, along with their material composition, synthesis strategies and intrinsic properties. Methods to improve the functionalities of materials are summarized. Following that, the state-of-the-art soft robotic applications based on these functional materials are highlighted. Finally, we conclude with a prospective outlook in terms of future trends of stimuli-responsive materials in soft robotics.

2. Stimuli-responsive materials

2.1 Dielectric elastomers

Dielectric elastomers (DEs), one representative class of electroactive materials, have been widely used as actuators in soft robotic systems, since Pelrine *et al.* firstly demonstrated that external voltages applied to acrylic elastomers (3M VHB) can generate large strain (greater than 380%) in 2000.[16] A basic form of dielectric elastomer actuator (DEA) is shown in Fig. 2a, where compliant electrodes sandwich a dielectric film. When a high voltage is applied to the electrodes, an electric field will be generated between the electrodes. The induced Maxwell stress leads to the area expansion and thickness shrinkage of the elastomer. The structure of a DEA can be simply taken as a compliant capacitor. The electric energy is directly and freely transformed to mechanical energy, and *vice versa*, leading to DEAs' advantages of compact structure and rapid response. To date, DEs have been devised into various configurations in soft robotic applications.[8,17]

In soft robotic applications, the level of voltage-induced strain represents one of the most significant performance indicators. The mechanics theory of DEs has been well established, as summarized in Suo's review.[18] The voltage-induced Maxwell stress s and strain ε can be expressed by

$$s = \varepsilon_0 \varepsilon_r E^2 = \varepsilon_0 \varepsilon_r \left(\frac{V}{h}\right)^2 \quad (1)$$

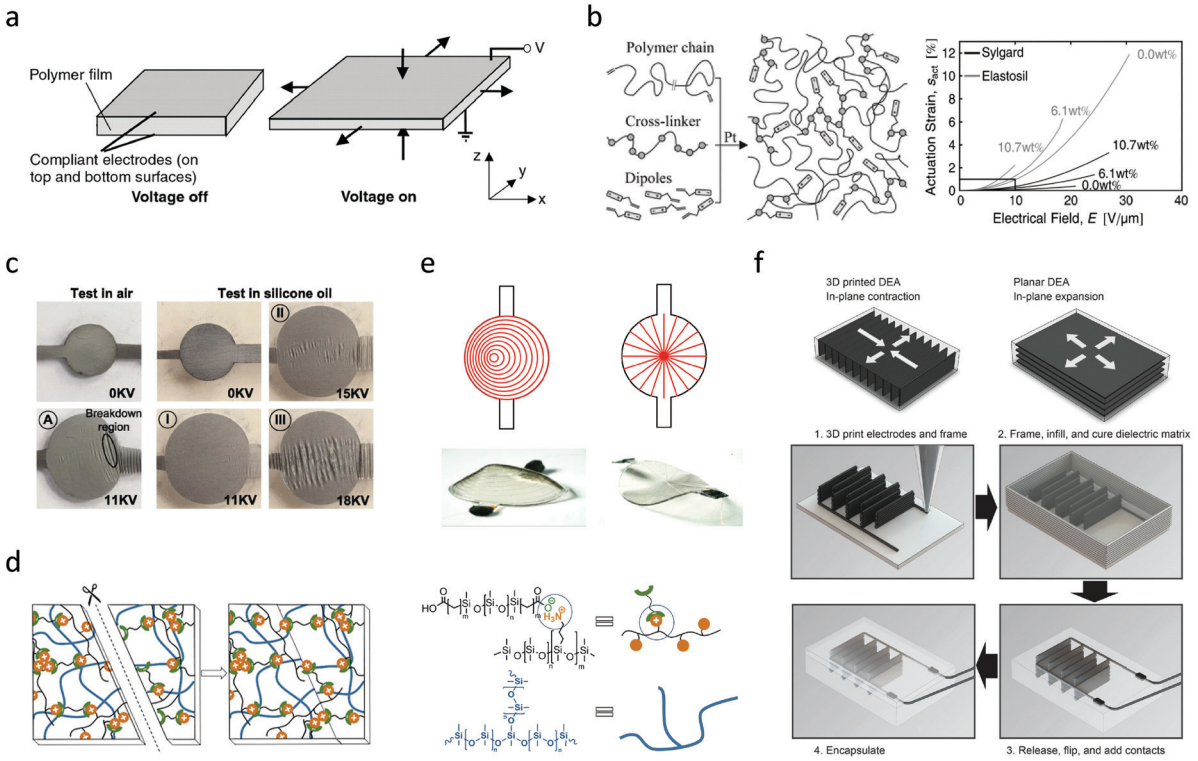

Fig. 2 Dielectric elastomers (DEs) as stimuli-responsive materials. (a) Working principle of a DEA. Reproduced with permission.[16] Copyright 2000, AAAS. (b) The actuation strain of Sylgard and Elastosil films varies with the number of dipoles. Reproduced with permission.[25] Copyright 2012, Royal Society of Chemistry. (c) The voltage-induced deformation of DEAs immersed in air or oil. Reproduced with permission.[30] Copyright 2013, AIP Publishing. (d) Chemistry of the prepared interpenetrating polymer networks for self-healing DEAs. Reproduced with permission.[32] Copyright 2016, American Chemical Society. (e) DEAs with 3D printed stiffening elements. Reproduced with permission.[38] Copyright 2019, Elsevier. (f) Printed DEAs with interdigitated electrodes and dielectric matrix infilling. Reproduced with permission.[42] Copyright 2020, Wiley.

$$\varepsilon = \frac{s}{Y} \tag{2}$$

where ε_0 is the vacuum permittivity, ε_r denotes the relative dielectric constant of the material, E is the electric field determined by the applied voltage V and the thickness of the actuated elastomer h, and Y denotes the Young modulus. The electric field E cannot exceed the critical breakdown strength (also referred to as the dielectric strength). To improve the electromechanical performance of DEAs, researchers have investigated various material systems and made modifications using material and structure engineering, as discussed in the following.

Common materials for DEAs can be divided into three categories: polyurethanes (PUs), acrylics and silicones. Each material system has its own advantages and disadvantages. PUs generally have higher dielectric constant and larger force outputs, and require lower electric fields for actuation. Meanwhile, PUs have higher elastic modulus, partly due to the crystallization at the microscopic level,[19] leading to relatively small strain. Acrylic DEs are more advantageous in terms of producing large voltage-induced strain. The commercially available 3M VHB acrylic elastomers are mostly used for generating large deformation, *e.g.* linear strain over 380%[16] and area strain over 2200%.[20] However, the viscoelastic nonlinearities in acrylic elastomers affect the overall performance and repeatability, requiring effective control strategies to compensate.[21,22] Silicone-based DEAs exhibit moderate actuation strain, mainly due to the smaller dielectric constant of silicones. Notably, the viscosity loss of silicone elastomers is much lower than that of acrylics, allowing for operation at higher frequencies and in a broader temperature range with less heat generation.[23] The inherent stability of silicone elastomers leads to repeatable and reproducible actuation upon activation. Rosset *et al.* dictated the fabrication process in detail.[24]

Given the relations in eqn (1) and (2), researchers have made continuing efforts toward improving the electromechanical strain by developing materials with high dielectric constant and strength. Materials scientists have made many attempts to enhance the dielectric constant, by introducing extra components into the dielectric matrix, such as organic dipoles,[25,26] and conductive nanofillers.[27,28] For example, Risse *et al.* chemically grafted strong push–pull dipoles to silicone elastomer networks in the film formation process (Fig. 2b), leading to the increase of the permittivity at all frequencies, at the expense of the decrease of the dielectric strength and the material modulus.[25] Fig. 2b also shows that the resulting maximal actuation strain is a trade-off between these effects, and it is material-specific. Fiorido *et al.* introduced a PU matrix containing Fe_3C-based nanofillers fabricated by electrospinning, the permittivity increased remarkably at all frequencies, and the deflection strain upon activation was greatly improved.[28]

Researchers have also made great efforts to enhance the dielectric strength of DEAs. Huang *et al.* found that the dielectric strength increases with the stretching level.[29] This is part of the reason why DEAs are typically provided with some level of prestretch.[29] La *et al.* further found that an enhancement of the dielectric strength up to 800 MV m^{-1} (450 MV m^{-1} in air) was achieved when a DEA (3M VHB) was immersed in silicone oil (Fig. 2c).[30] The inherent reason is that the thermally conductive silicone oil stabilizes the temperature of the dielectric material, alleviates local thermal runaway, and thus maintains electrical insulation. In consideration of applications that require dynamic stimuli, researchers also found that the dielectric strength is insensitive to the frequency of the applied voltage.[31] A direct solution to increasing the lifetime of DEs is to develop self-healable elastomers which can maintain functions after detrimental damage such as tearing or electrical breakdown. For example, Madsen *et al.* introduced interpenetrating polymer networks of silicone elastomer and ionic silicone species, and the ionically cross-linked silicone provided self-healing properties due to the reassembly of the ionic bonds (Fig. 2d).[32] The recovery of the strain and stress after self-healing is highly material specific, and it still requires further research endeavors for developing various types of self-healable DEs. The self-healing ability is advantageous to enhance the high-voltage cyclic stability and robustness of DEs in harsh environments.

Compliant electrodes also have an important impact on the functionality of DEAs. Generally, the electrodes are expected to possess the properties of good conductivity, compliance (on par with the dielectric material), and robustness to bond with DEs. Common materials for electrodes in DEAs include carbon grease, graphite, carbon powder, and carbon nanotubes (CNTs). Carbon grease is widely used because it is highly compliant, conductive, and easily accessible. La and Lau further encapsulated carbon grease to improve the thermal stability and thus enhance the dielectric strength.[33] CNT-based electrodes are preferential for multi-layer stacked DEAs because they are very thin, leaving a sufficient gap for adhesion between adjacent layers of DEs.[34,35] The advantageous properties of optical transparency[36] and self-healing[37] of ionic electrodes (*i.e.* hydrogels) are also preferential in some applications such as camouflage.

The aforementioned chemical or material-level modifications to DEs and electrodes frequently lead to a compromise in properties. For example, when the dielectric constant increases, the dielectric strength usually decreases. In addition to these modifications, structure engineering of DEAs also represents an effective approach to improve their electromechanical performance. For example, Hajiesmaili *et al.* printed a set of concentric, stiff fibers onto multilayer DEs for morphing the flat sheets into conical shapes upon activation (Fig. 2e), and the fiber patterns can be inversely designed to generate desired shapes.[38] The same group also achieved the same goal by applying a spatially-varying electric field through patterning gradient electrodes across the multilayers.[39] This innovative approach leverages well the freeform design of electrode patterns to modulate the actuation fields and thus the induced displacement field. Furthermore, a more general approach was provided by Chen *et al.* to automate the electrode pattern design by using a level-set-based topology optimization approach.[40]

In general, the design of DEs with arbitrary shapes calls for compatible fabrication techniques. Therefore, 3D printing of DEs and electrodes has also been a topic of interest. Poulin *et al.* developed a process based on pad printing, which can directly patternize μm-thick silicone films and electrodes with an amorphous geometry at a resolution of 100 μm.[41] The ultrathin membrane also greatly reduced the operation voltage (below 300 V). Recently, Chortos *et al.* provided a more general fabrication solution of DEAs with no need for prestrain, by encapsulating printed and cured interdigitated vertical electrodes within a dielectric matrix (Fig. 2f).[42] This technology allows DEAs to be produced in nearly arbitrary geometries, enabling unprecedented design flexibility for DEAs, but the limitations of dielectric strength (25 MV m^{-1}) and actuation strain (9%) need to be improved.

2.2 Hydrogels

Hydrogels are crosslinked polymeric networks with high water content that construct most living tissues and inspire various biofunctional applications.[7,13,43–45] In contrast to other soft materials, the hybrid structure composed of water molecules and polymer networks endows hydrogels with coupled features of a liquid and solid. They can respond to multiple physical or chemical stimuli and exhibit versatile properties across the liquid–solid states. Since the biological use of hydrophilic gels was first presented in the 1960s,[46] synthetic hydrogels have been rapidly developed, leading to broad prospects in bionic devices and machines. Furthermore, due to their unique attributes such as inherent softness, stretchability, transparency and biocompatibility, hydrogels have emerged as attractive stimuli-responsive building block materials for making soft robotic systems like sensors and actuators.

According to different responsive elements, the stimuli-responsive mechanisms of hydrogel devices can be generally classified into two basic categories, including active responsive hydrogels and passive hydrogel matrices incorporated with responsive substances. Active responsive hydrogels undergo volume and/or phase changes when exposed to external stimuli including physical (temperature, light, electric fields, and mechanical forces)[47–50] and chemical (pH and ions)[51–53] inputs. The transitions of volume and/or phase depend on molecular level changes and rearrangements of polymer chains and networks in hydrogels. For example, thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) hydrogels have been commonly used to detect changes in environmental temperature.[7] The polymer chains undergo a transition from coils to globules when the temperature decreases below the lower critical solution temperature, while the macroscopic shape of the hydrogels obviously shrinks. Based on the isotropic changes in hydrogels, Yu *et al.* further investigated PNIPAM hydrogels capable of programming deformations in anisotropic geometries *via* embedded serpentine mesh layouts as microheaters, leading to an extended responsive pattern (Fig. 3a).[47] In addition to

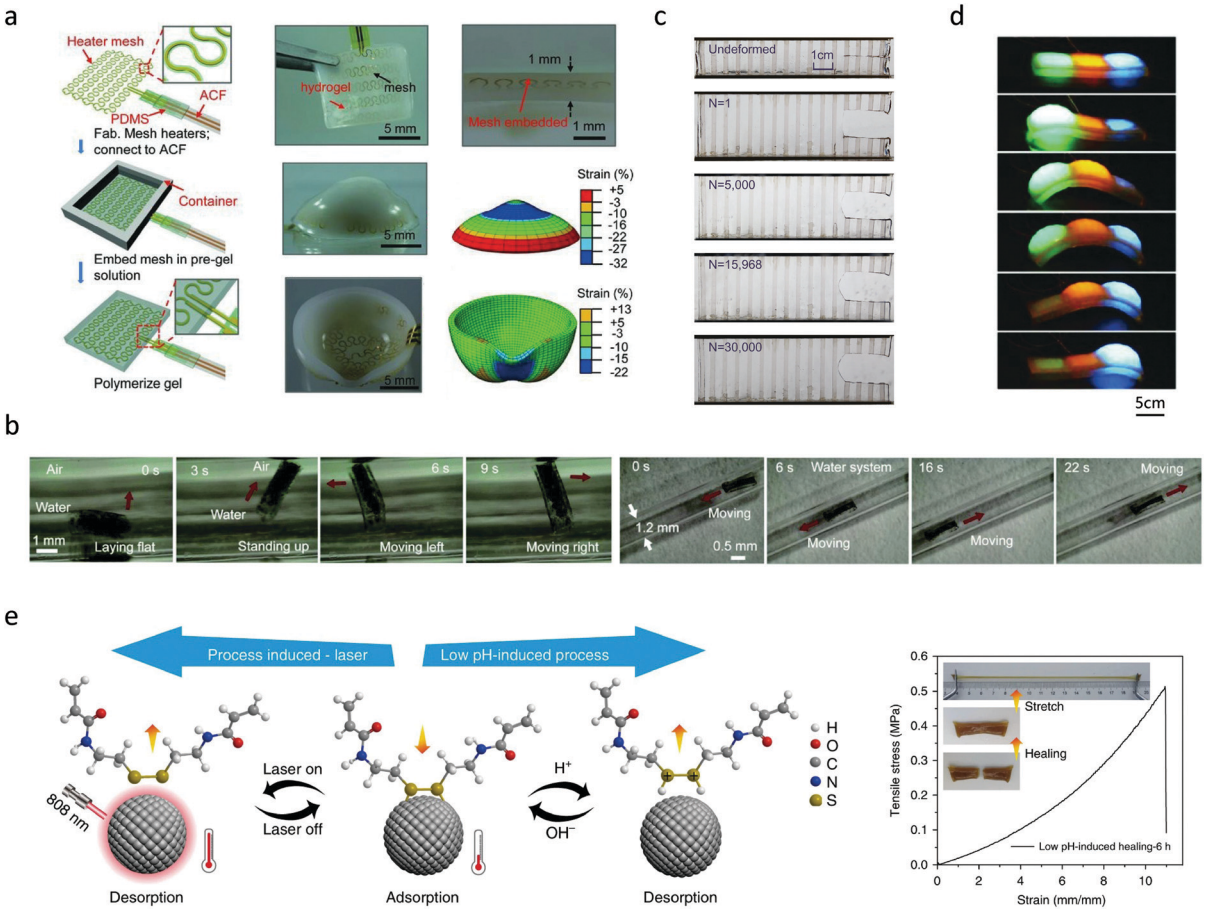

Fig. 3 Hydrogels as stimuli-responsive materials. (a) Thermoresponsive PNIPAM hydrogels integrated with ultrathin compliant electronic meshes enabling reversible programming of spatially non-uniform 3D shapes. Reproduced with permission.[47] Copyright 2013, Wiley. (b) A magnetically responsive hollow hydrogel robot capable of jumping (left) and changing the direction of movement (right). Reproduced with permission.[65] Copyright 2019, Royal Society of Chemistry. (c) Hydrogels with a crack survive over 30 000 cycles of loading and exhibit a high amplitude of the energy release rate of ~1290 J m^{-2}. Reproduced with permission.[68] Copyright 2019, Elsevier. (d) Pneumatic robots with electroluminescent hydrogel skins change the luminescence when the skin is stretched in locomotion. Reproduced with permission.[56] Copyright 2016, AAAS. (e) Schematic illustration and performance of the self-healing ability of one hydrogel composite relying on dynamic thiolate–metal coordination as healing motifs. Reproduced with permission.[69] Copyright 2019, Springer Nature.

active hydrogels composed of pure polymeric networks, hydrogel matrices hosting responsive elements are also synthesized. These active substances are either physically inserted or chemically anchored to the polymeric networks and respond to signals in external environments, while the network structures act as passive containers. One classical example was that polyacrylamide (PAAm) hydrogels containing NaCl were used as ionic electrodes to construct crucial components of resistive strain sensors.[54] The external mechanical strain results in corresponding changes in the resistance of the hydrogel electrodes.

Over the years, a wide variety of design strategies have been explored based on the above principles to expand the value of hydrogels in practical robotic systems. As a typical method, constructing double networks of hydrogels enables brittle materials to overcome the fragility. Alternatively, multilayer-structure, patterning design, and crosslinking gradients have also been used to tune their comprehensive performances.[4,55]

Regarding responsive substances incorporated with polymer networks, the diversity of these entities provides abundant options for developing favorable properties of hydrogels. The range of these substances mainly involves free ions,[54,56] nanofillers,[57–61] and conducting polymers.[62,63] For instance, hydrogel matrices accommodating salt ions like NaCl and LiCl are endowed with reliable ionic conductivity and can gelatinize *via* simple fabrication methods.[54] Nanomaterials like graphene,[57] CNTs,[58] AgNWs,[59] and MXenes[60,61] inserted into hydrogel networks are capable of introducing impressive features in the electrical, mechanical, and electrochemical fields. Also, conductive polymers such as PEDOT:PSS blended with pure hydrogels are promising electrical interfaces for stimulation and biofunctional use.[62] Naficy *et al.* reported a 3D printed pH-responsive hydrogel based on PEDOT doped with PSS and hydrophilic PUs.[64] The proposed biosensor can withstand large deformations without significant deterioration of the electrical capabilities. Magnetic particles can be added to

yield magnetically responsive hydrogels, which are utilized for remote soft actuating and morphology control. Liang *et al.* recently reported a type of hollow hydrogel microfibers loaded with magnetic materials.[65] The reported non-coaxial microfluidic method can fabricate hydrogels with sophisticated geometries, potentially applied as a vascular scavenger (Fig. 3b). Novel structural design strategies of hydrogel composites have also developed hydrogel-based devices responding to chemical stimuli. For example, polyvinyl alcohol (PVA) and polyvinylidene fluoride (PVDF) have been demonstrated to construct bilayer structures with microchannel patterns that respond to acetone vapours, which can be used to actuate dynamic elements.[66]

The exceptional physical and chemical properties of hydrogels are significant in their extensive uses for soft robotics. Hydrogels possess intrinsic softness and conformability with tuned elastic moduli mostly from 1 kPa to 100 kPa, which exactly lie in the range of materials constructing soft robotics.[1,13] The resultant compliance matching is particularly crucial to prevent mechanical irritation and physical interferences between components. Meanwhile, the stretchability and toughness enable hydrogel-based devices to adapt to general working conditions when applied in strain sensors and artificial muscles. Hence, intensive efforts have been made to improve the elastic limit in tension. Suo and co-workers reported that a hydrogel mixed with two types of crosslinked polymer can be stretched to 2000% of its initial length and simultaneously possesses high fracture energies of $\sim$9000 J m^{-2}.[67] Recently, Suo and co-workers further proposed a principle of stretchable and fatigue-resistant hydrogels by embedding unidirectional fibers into a polymer matrix and adhering these two elements through sparse and covalent interlinks. The resulting PAAm–PDMS composites achieved a high threshold of 1290 J m^{-2} (Fig. 3c).[68] Besides the mechanical properties, hydrogels also present unique transparency. Some ionic hydrogels are transparent in the complete visible spectrum, compared to other commonly used electrode materials such as ITO, AgNWs, SWNTs, and graphene.[13] These transparent, stretchable, and conductive hydrogels can be used as electrodes in optoelectronic devices such as electroluminescent skin with visual sensory feedback (Fig. 3d).[56] Additionally, some hydrogels exhibit self-healing ability when damaged, which is typically found in biological tissue. For example, a hydrogel with a highly-ordered lamellar network crosslinked by metal nanostructure assemblies is autonomously self-healable, suitable for constructing robust soft robots under extreme working conditions (Fig. 3e).[69]

Potential challenges of synthetic hydrogels for soft robotics consist of water retention and reliable adhesion to diverse elastomers and solids. Hydrogels with high water content are prone to dehydration in low ambient humidity, which limits their robust and long-term use in robotic devices. Methods such as incorporation of moisturizing fillers and coating layers have been reported to slow down the water loss and maintain the initial properties.[70] However, more effective water retention approaches require further exploration. Strong adhesion of hydrogels prevents delamination and benefits integration with other dielectrics, seals and solid interfaces. Various design strategies like physical or chemical interactions, surface modification and gluing methods can be introduced to enhance the adhesion.[13] For example, a promising solution is to chemically anchor the long-chain polymer networks of hydrogels covalently to non-porous solid surfaces.[71] Notably, it is also of significance to avoid compromising the intrinsic stretchability and conformability of hydrogels.

2.3 Shape memory polymers

Responsive materials capable of being programmed to arbitrary shapes and recovering memorized shapes are commonly referred to as shape memory materials.[6] These materials with the shape memory effect under specific external stimuli such as heat[72,73] and light[74] have been developed based on various classes of materials, including alloys, ceramics, and polymers.[5] Shape memory polymers (SMPs) present notable advantages over conventional rigid materials due to their intrinsic softness and conformability. Compared to other types of soft stimuli-responsive materials, SMPs also exhibit unique applicable features. For example, hydrogels are unsuitable for extremely dry working conditions and tend to undergo stimuli-induced swelling/deswelling, while SMPs are not limited to moist atmospheres and can achieve directed motions beyond expansion and shrinking.[4,6] Thermo responsive SMPs have been extensively explored in contrast to other external stimuli. Since the 1960s, SMP based heat-shrinkable tubing has been widely used to insulate bare wires in industry.[6] Over the past decades, SMPs with complex morphology designs and reversible shape transformations have been further applied in soft robotic actuators and other structural components.

The responsive principles of SMPs can be classified into the one-way effect and the two-way effect. A one-way effect based SMP can form a temporary shape under external stress when heated to a temperature T_{reset}. After removal of the applied stress, the unstable shape is fixed upon the decrease of the temperature to T_{low}. When the environmental temperature is elevated over T_{reset} again, the recovery to the original shape is elicited and a programmable process of the one-way shape memory effect is completed. From a molecular level perspective, SMPs are composed of polymeric networks with chain segments. The macroscopically programmed process corresponds to macromolecular chain orientation, inducing vitrification or crystallization of the material. Researchers have developed a wide variety of functional structures and programmable shape deformations based on one-way SMPs. Wang *et al.* reported 3D printed horseshoe lattice structures with commercial SMP Vero (an acrylic-based photopolymer). The complex controlled shape changes are analyzed by a phase evolution model that considers the geometrical nonlinearity and the material nonlinearity of SMPs (Fig. 4a).[75] In addition, more than one memorized temporary state can be realized through tuning the network structure and chemical composition, which is referred to as the multi-state shape memory effect (Fig. 4b).[76] Nevertheless, conventional one-way effect based SMPs are unable to support reversible shape changes, leading to a limit to their practical applications.

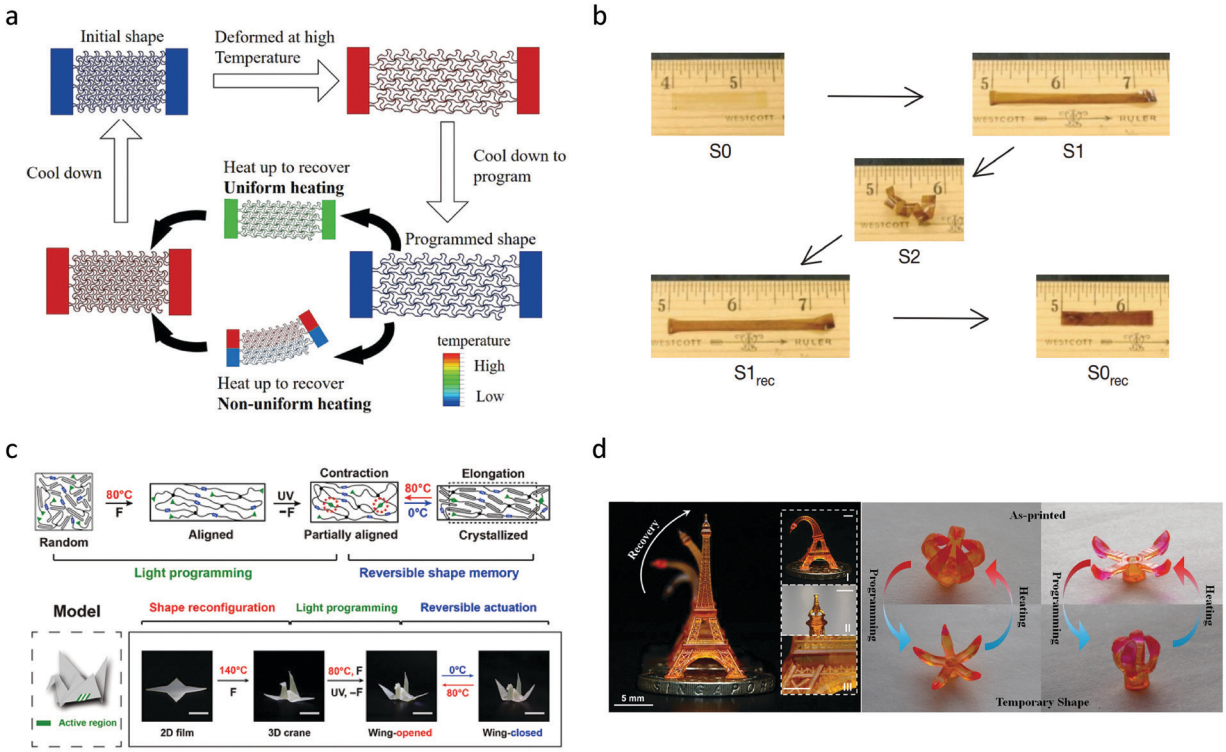

Fig. 4 Shape memory polymers (SMPs) as stimuli-responsive materials. (a) Shape memory cycle of 3D printed SMP based lattice structures with various intermediate states controlled by the thermal stimuli distribution. Reproduced with permission.[75] Copyright 2020, American Chemical Society. (b) Triple-shape memory effect of the perfluorosulphonic acid ionomer (PFSA). Reproduced with permission.[76] Copyright 2010, Springer Nature. (c) Mechanism for reversible shape memory behavior *via* photo-programmed actuation (top) and a polycaprolactone–polyurethane-based 3D crane capable of yielding reversible flapping (bottom). Reproduced with permission.[78] Copyright 2018, AAAS. (d) A multimaterial 4D printed system that can create complex 3D shape memory structures with a single SMP (left) and multiple SMPs (right). Reproduced with permission.[73] Copyright 2016, Springer Nature.

Recently, the developed two-way SMPs have gradually attracted much attention since they can provide continuously reversible shape memory actuation without the need for additional external stress.[4,77] Two-way SMPs consist of two functional domains, including an actuation domain and a geometry determining domain. These two structural units with different melting transition ranges provide the actuation force and determine the programmed deformation, respectively. After programming and forming a temporary shape at T_{low}, the material can be transformed into a partially recovered original shape upon heating to T_{sep}, which is above the melting transition range of the actuation domain and below that of the geometry determining domain. A reversible shape change from the partially recovered shape to the temporary shape can be realized through cyclic thermal testing between T_{sep} and T_{low}. Finally, the material is completely recovered to the initial shape upon heating to T_{reset}. For instance, Jin *et al.* demonstrated a polycaprolactone–polyurethane-based two-way network containing both thermo- and photo-reversible bonds. A planar polymeric sheet can be programmed to a 3D crane shape through a thermal response. After activating the active region *via* UV light, reversible flapping of wings is elicited upon continuous heating–cooling cycles (Fig. 4c).[78]

Versatile stimuli-responsive properties enable SMPs to be an emerging material candidate particularly for soft robotic actuation. Besides the inherent softness feature, SMPs possess stiffness-tunable capability with a two-to-three order of magnitude change of the elastic moduli.[4,79] Reversible stiffness tunability is of great significance in soft robotic systems that overcome the limits of low load capacity and narrow stiffness range.[72] Moreover, programmability and reprogrammability of SMPs are crucial for the realization of predesigned morphology and arbitrary reconfiguration. Microscopic structures and compositions can be fine-tuned to induce programmed motions related to actuation behaviors such as bending,[73] twisting,[76] folding,[78] and stretching.[80] From the viewpoint of fabrication methods, the concept of 4D printing has been recently presented to facilitate the manufacturing viability of SMP based actuators, which combines the ubiquitous technologies of 3D printing and shape memory polymeric materials. Ge *et al.* developed a high resolution multimaterial 4D printing method capable of printing tailorable SMPs (Fig. 4d). Desired thermo responsive properties were demonstrated through the precise control of the chemical constituents and compositions of the printed materials.[73]

Future developments on SMPs should overcome the slow transition speed and hysteresis.[11,79] The response time is related to the inherent properties of the materials and also influenced by the external heating/cooling process. A potential solution is to optimize the configurations of thermal systems. For example,

a fluidic microchannel cooling system significantly reduces the thermal response time of SMP based actuators, compared to conventional convection cooling approaches.[72] Moreover, the spatial localization of the response is significant to the complexity of the morphology and diversity of actuation behaviors. For instance, non-uniform thermal stimuli can be applied in the recovery stage to induce bending motions as an intermediate shape.[75]

2.4 Liquid crystal elastomers

Liquid crystal elastomers (LCEs) represent a new type of thermoplastic elastomer that uses liquid crystal molecules as a physical crosslink, which combines the entropy elasticity with self-organization properties.[81] At the molecular level, the liquid crystal (LC) exhibits long-range orientational or positional organization. By virtue of changing the orientation order of an LC unit and the entropy elasticity of the polymer network, LCEs could obtain the dual properties of self-organization and intrinsic softness, enabling large deformation responses to external stimuli.[12,82] LCEs have many excellent properties, such as large deformation, shape memory,[83] and self-healing ability,[84] making LCEs promising actuation technologies in the field of soft robotics.[12,85]

Generally, the stimuli-responsive mechanisms of LCEs can be divided into several main categories: photo-,[86] thermo-,[87] photothermal-[88] and photochemical[85] induced LCEs. LCEs typically exhibit rather large deformation but their backbone is soft, leading to small output forces under actuation. All LCEs are sensitive to the change of temperature. Near the phase transition temperature, LCEs reversibly transit from an ordered and anisotropic phase (elongated) to a disordered and isotropic phase (shrunk). In 1981, the world's first LCEs were synthesized by Finkelmann *et al.*, and when heated the LCEs contracted and showed a 26% shrinkage strain.[89]

In photo-induced LCEs, photo-induced isomerization is mainly induced by photochromic molecules such as azobenzene (AZ).[90] During this process, the stable *trans*-isomer of AZ molecules was transformed into the metastable *cis*-isomer, leading to the transition of LCs into an isotropic state. SWNTs,[88] polydopamine[91] and graphene oxide[92] can absorb NIR/IR light and photon energy is converted to thermal energy rapidly. Banisadr *et al.* reported that laminated films which combined a SWNT–LCE with elastomeric photonic crystals could acquire simultaneous reconfiguration of the surface color and morphology.[88]

LCEs are promising materials for next-generation artificial muscles owing to their compliant nature and reversible response to thermal stimuli. It was demonstrated that LCEs could produce actuation strains and stresses on a par with mammalian skeletal muscles.[91] For thermo responsive LCEs, heating elements are usually integrated into the elastomer in practical use of LCEs,[93] but the heating wires may constrain the stretchability of the material. Besides, the cooling process is generally challenging to implement and control. He *et al.* fabricated artificial muscles by integrating internal fluidic channels into LCEs and demonstrated excellent actuation performance in a broad range of environmental temperatures.[94]

For broader applications in soft robotics, many efforts have been made to enhance the performance of LCEs, characterized by complex deformation behaviors and an ability of producing sufficient actuation force. Kim *et al.* developed a strategy that enables programmable, multi-responsive shape morphs of composites comprising carbon nanotubes in LCEs, driven by visible light or electric currents (Fig. 5a).[95] Liu *et al.* developed a two-step acyclic diene metathesis by the polymerization/crosslinking method which resulted in a material with extraordinary photothermal conversion property and excellent load capability (Fig. 5b).[96] Donovan *et al.* designed a 2D pattern of an LCE-film and developed an origami pattern that can open or close, controlled with light, which extended the ability of LCEs to accomplish complex 3D bending (Fig. 5c).[97] Iamsaard *et al.* have developed LCE-springs that undergo complex motion behaviors such as winding and unwinding under UV light (Fig. 5d).[98] Similarly, inspired by plant tendrils, Wang *et al.* designed an LC actuator that mimicked plant tendrils by a polysiloxane-based dual layer structure, which could achieve 3D reversible deformations (bending/twisting) by simply varying the wavelength band of light (UV/NIR).[86]

The self-healing ability of some LCEs is also preferential for soft robots that are susceptible to mechanical damage in unpredictable environments. Zhong *et al.* produced novel liquid crystalline copolyesters based on AZ and biphenyl group mesogenic units by one pot melt polycondensation. These copolyesters could be reshaped and reprocessed without chemical crosslinks.[99] By virtue of disulfide bonds, Wang *et al.* fabricated a novel LCE capable of transitioning from the polydomain phase to the single-domain phase *via* heating or UV light. In addition, this LCE has the ability to self-heal by heating.[100]

2.5 Magnetic materials

Magnetic fields represent another powerful resource for actuation of soft robots, with advantages of large distance, dexterity, precision, high speed and robustness. In particular, magnetic fields enable safe and deep penetration into the human body, and thus exhibit unique potential for empowering soft robots in biomedical applications such as drug delivery, diagnosis, and non-surgical therapy: they provide far-field actuation with untethered control, which increases the safety and efficiency during medical operation.[101,102] Magnetically responsive materials are at the core of the development of soft robots that can, under external magnetic fields, deform largely, navigate within complex workspaces, and perform specific tasks.

Fundamentally, the response of a material to an external magnetic field can be described as diamagnetic, paramagnetic, ferromagnetic or antiferromagnetic, among which ferromagnetic materials are preferential because dipole moments induced by a magnetic field are retained even after the magnetic field is removed. Ferromagnetism in nature exists in iron, nickel, cobalt and their alloys. Ferrimagnetism is similar to ferromagnetism except that the materials contain diamagnetic elements such as oxygen, leading to reduced magnetization.

In terms of the coercivity, which captures the resistance of a magnetic material to changes in magnetization, ferro- and

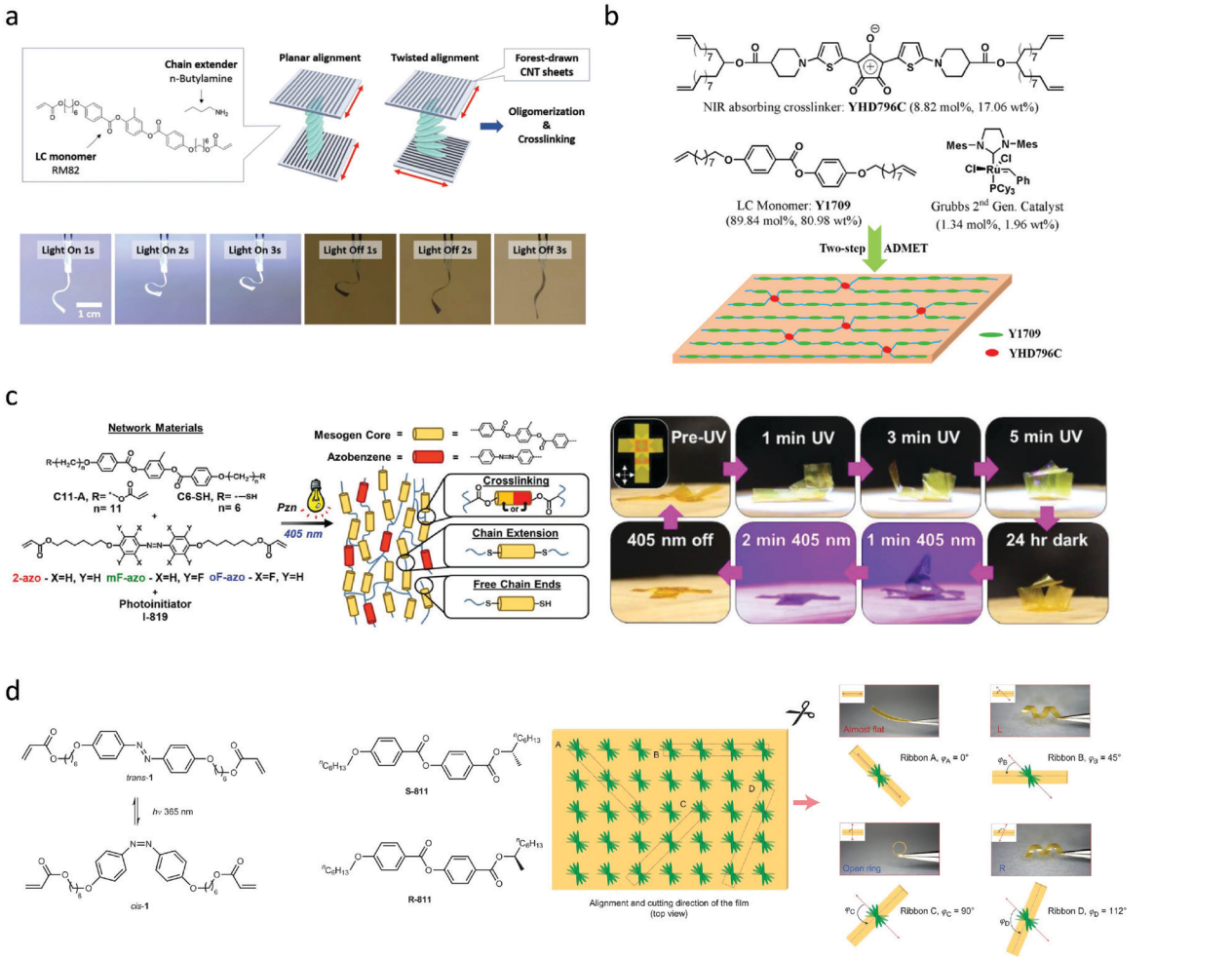

Fig. 5 Liquid crystal elastomers (LCEs) as stimuli-responsive materials. (a) Molecular structure of the monomers used and the fabrication scheme used to prepare LCE/CNT composites (top). Time-lapse optical images of programmed S-shape bending actuation of a lay-up-patterned LCE/CNT composite film in response to visible light (bottom). Reproduced with permission.[95] Copyright 2019,Wiley. (b) Chemical composition of the thermally-induced LCE material with a high photothermal conversion property. Reproduced with permission.[96] Copyright 2017, American Chemical Society. (c) Chemical structures and synthesis of AZ-based LCEs (left) and the optical control to achieve 3D configurations (right). Reproduced with permission.[97] Copyright 2019, Wiley. (d) Chemical structures of the molecular photoswitch and chiral dopants S-811 and R-811 for the photo-induced LCEs (left), and the ribbons of various 3D shapes by tuning the cutting direction (right). Reproduced with permission.[98] Copyright 2014, Springer Nature.

ferri-magnetic particles fall into two categories, soft and hard magnets. Soft-magnetic materials featuring low-coercivity do not adequately reserve the magnetism after the dissipation of the magnet field, and common examples include an Fe–Si alloy and Fe–Al series of alloys. Some simple but limited actuation could be achieved. Kawasetsu *et al.* designed a tactile sensor capable of measuring both normal force and compression using a magneto-rheological elastomer embedded with carbonyl iron particles, where the magnetorheological elastomer sheet tailors the magnetic flux through the magnetic transducer.[103] Highly-magnetic materials featuring high-coercivity such as neodymium–iron–boron (NdFeB) exhibit high remnant magnetism characteristics, and are more preferential in robotic applications because their relatively stable magnetism allows directly amendable magnetic fields to create programmable robotic behaviors.

To enable soft robotic applications with magnetic actuation, in general one needs to embed magnetic particles into mechanically soft matrices. The most common magnetic materials include hard neodymium–iron–boron particles,[104–106] superparamagnetic iron oxide particles,[107,108] CrO_2 powder[109] *etc.* From the perspective of actuation, the magnetization property of the materials and their volume assume significant roles at the stage of design, by to a large extent determining the output forces and torques.[101] An initial step is to embed discrete permanent magnets into soft matrices. For example, for steering during intravascular treatments, Jeon *et al.* attached a soft magnetic microrobot, of which the magnetization direction and intensity can be modulated, to the end of a flexible guidewire (Fig. 6a).[110] The microrobot features soft bodies consisting of polydimethylsiloxane (PDMS) and two neodymium magnets (NdFeB, N52). Kwok *et al.* developed modular magnetic robots with soft and hard parts, and NdFeB ring magnets were embedded to function as controllable connectors between different parts.[111]

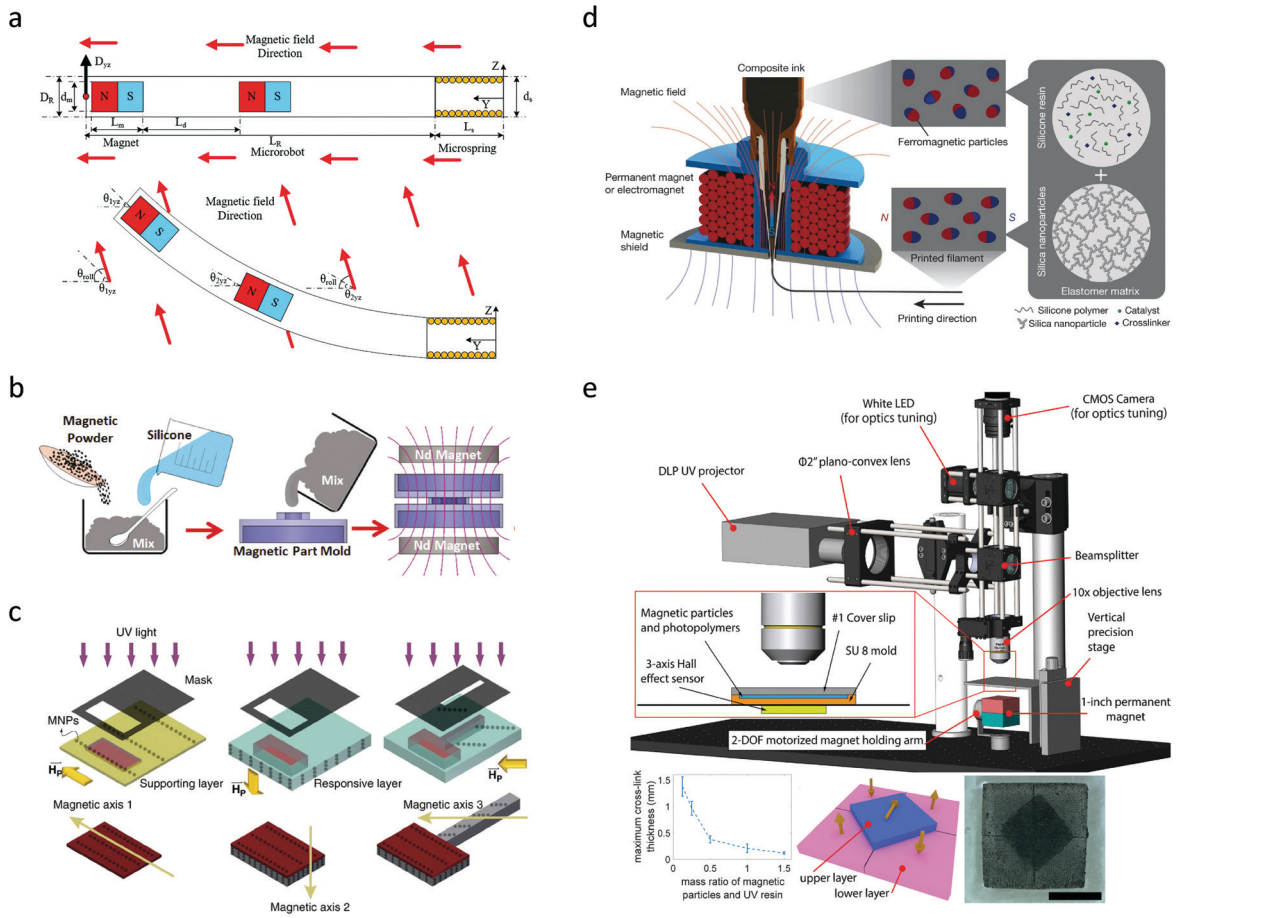

Fig. 6 Soft magnetically responsive materials. (a) A magnetic microrobot capable of steering the guidewire in response to external magnetic fields. Reproduced with permission.[110] Copyright 2019, Mary Ann Liebert, Inc. (b) Fabrication process of the soft sensor with embedded magnetic powders. Reproduced with permission.[112] Copyright 2019, Elsevier. (c) The fabrication process of soft biomimetic micromachines including photopatterning of microstructures, and infilling of magnetic particles. Reproduced with permission.[115] Copyright 2016, Springer Nature. (d) Schematics of the printing process during which the encoded ferromagnetic particles are redirected by an external magnetic field. Reproduced with permission.[104] Copyright 2018, Springer Nature. (e) The setup for patterning 3D magnetization in UV-curable elastomers. Reproduced with permission.[116] Copyright 2019, AAAS.

By mixing magnetic particles evenly in the polymer and magnetizing the mixture during the curing process, an isotropic distribution of magnetization could be achieved. Examples include soft sensors[112] (the fabrication process shown in Fig. 6b) and artificial skins.[113] However, the isotropic magnetization poses a challenge for creating complex actuation modes compatible with soft-bodied robots, which typically requires complicated design of spatially-varying magnetic fields. With the development in magnetic field control[114] and compatible fabrication methods, soft materials encoded with nonuniform magnetization are achievable, greatly releasing the design freedom to generate more complex robotic behaviors that are otherwise hard to realize.[105] As shown in Fig. 6c, Huang *et al.* developed a soft self-folding microrobot with complex body arrangements and controllable locomotion, enabled by embedded magnetic nanoparticles (MNPs) with tunable alignments. The mechanical design can be reprogrammed selectively and the body parts have anisotropic magnetism, allowing for the flexible modulation of the motion behaviors.[115] Lum *et al.* developed a universal design method to automate the generation of the needed magnetization profile and the spatially-varying actuation field for soft matter to morph to desired configurations.[106] The presented design theory is in general applicable to 3D shape-morphing, but the fabrication was limited to producing planar beams.

Recently, Kim *et al.* proposed a new fabrication method by reorienting the polarities of deposited inks on the microscale and encoding a 3D structure with a pattern of ferromagnetic domains on the macroscale, as shown in Fig. 6d.[104] This ink was made by mixing non-magnetized NdFeB particles in an uncured elastomer matrix and magnetizing the particles in the extrusion channel with a controllable external magnetic field. Since the printing process is operated layer by layer, the magnetization direction can only be aligned with the filament lengthwise direction. Xu *et al.* further improved the fabrication flexibility through UV lithography. By controlling the orientation of magnetic particles and selectively exposing them to UV light, magnetic particles were embedded inside in-plane materials with tunable 3D directions (Fig. 6e).[116] To enhance the biocompatibility, the possible corrosion of elastomers

embedded with iron particles needs to be addressed. Surrounding the magnetic particle with a silica layer proved to be an effective solution.[10] Furthermore, the covering of the hydrogel reduces the surface friction and avoids possible corrosion caused by magnetic particles during interaction with human vascular walls or tissues.

3. Applications of stimuli-responsive materials in soft robotics

3.1 Locomotion

Mobility is a fundamental function of robots, with various types of gaits such as crawling, climbing, walking, running, jumping and flying, with the support of the environment. These motions of different gaits are generally referred to as locomotion. Different from conventional rigid robots that rely on accurate control of joints to produce forces and move the center of mass of the robot, soft robots take inspiration from biology and generate motions mainly through their (actively) deformable bodies.[117] The aforementioned stimuli-responsive materials have been used to construct soft robots that can deform and undergo locomotion under external physical fields. The incorporation of these soft active materials is imbuing locomotive robots with new advantages such as light weight, compactness, low cost, safe interaction with the environment, and flexibility to navigate through unstructured and/or confined spaces.

Soft robot locomotion is largely characterized by the adopted actuation technology. The actuation technologies mentioned in Section 2 each have advantages and disadvantages, and thus are fit for specific applications. Compared to widely used pneumatic actuators in soft crawling[118] and navigation[119] robots that require rather bulky pumping devices, the compact DEA-based robots are preferential in confined environments. For example, Gu *et al.* developed an agile soft robot able to climb vertical walls and go through a confined tunnel by changing its body height, with multimodal locomotion such as climbing, crawling, and turning (Fig. 7a).[120] To decrease the applied voltage and eliminate the use of tethers, Ji *et al.* greatly improved the fabrication and integration technologies of DEAs to create freestanding locomotive robots driven by operating voltages below 450 volts (Fig. 7b).[121] They also integrated optical sensors, a microcontroller and a battery inside, and the whole robot weighs less than 1 g, which is otherwise hard (if not impossible) to realize. The rapid response of DEAs also extends their applicability in flapping-wing robots. Recently, Chen *et al.* developed a flying microrobot driven by multilayered DEAs with a resonance frequency of 500 Hz.[122] The authors also demonstrated that the resilience of soft materials allows multiple robots to survive collisions in a cluttered environment. The underwater locomotion of soft robots driven by DEAs was also reported.[123–125]

Soft robots that can move and navigate under magnetic fields show unique advantages in biomedical applications, where remote actuation and non-invasive access to confined and cramped spaces in bodies are typically required.[126] Hu *et al.* reported soft magnetic millimeter-scale robots which can transfer reversibly between liquid and solid domains, and with delicate control of external magnetic fields, switch between multiple modes of locomotion such as swimming in liquids, rolling and walking on solid surfaces, crawling through narrow tunnels and jumping over obstacles (Fig. 7c).[105] Kim *et al.* further explored the design space of soft magnetically responsive matter, in terms of the distribution and orientation of embedded magnetic particles, to create a new family of magnetic robots that can achieve multimodal locomotion under simple external fields (Fig. 7d).[104] Enabled by printable and programmable ferromagnetic matter in soft bodies, the same group also developed soft small-scale robots for performing steering and navigation tasks in confined environments like a model of brain vessels.[10]

Locomotion driven by other actuation technologies may bring additional benefits. For example, light stimulus has the advantages of being wireless, rapid, and scalable and having spatiotemporally selective capabilities. By incorporating polypyrrole nanoparticles as photothermal transducers, Luo *et al.* developed photo/thermo responsive composite hydrogels with controllable locomotion under NIR laser stimulation (Fig. 7e).[127] Based on thermo responsive CNT–SMP composites, an inchworm robot was designed that can achieve reversible actuation (Fig. 7f).[128] Palagi *et al.* demonstrated that, driven by structured monochromatic light, soft microrobots made of photoactive LCEs can achieve various biomimetic locomotion on demand (Fig. 7g).[129] This structured light stimulus is uniquely beneficial for locomotion that requires microscale actuation with sophisticated spatiotemporal coordination. Qian *et al.* further showed that LCEs based on allyl sulfide functional groups can perform repeatedly by reprogramming through light-controlled exchange reactions between the groups.[130]

Soft robotics is redefining the relationship between robots and the environment, in which an action results in dynamic responses among the bodies and the environment, requiring new design and control paradigms. As a fundamental function, the locomotion of soft robots requires a synthetic combination of actuation technologies, body design, gait design, environmental interaction, and control strategies, depending on specific applications. Material improvement in terms of the actuation strain, compactness, biocompatibility and other aspects will greatly explore the design space to realize better locomotion performance regarding the mode and speed of motion, adaptability, controllability, load capability, *etc.*

3.2 Grippers

Grasping and manipulation are effortless tasks for humans in everyday life. However, mimicking the dexterity and versatility remains challenging for bionic robots. Traditional robotic grippers comprised of rigid components rely on complicated design mechanisms and control strategies.[3] Particularly, the lack of softness leads to unsafe interactions when grasping deformable and fragile objects. In contrast to their rigid counterparts, soft grippers based on stimuli-responsive materials have attractive advantages including highly flexibility, conformability, and reconfigurability along with simpler designs.[11,131,132]

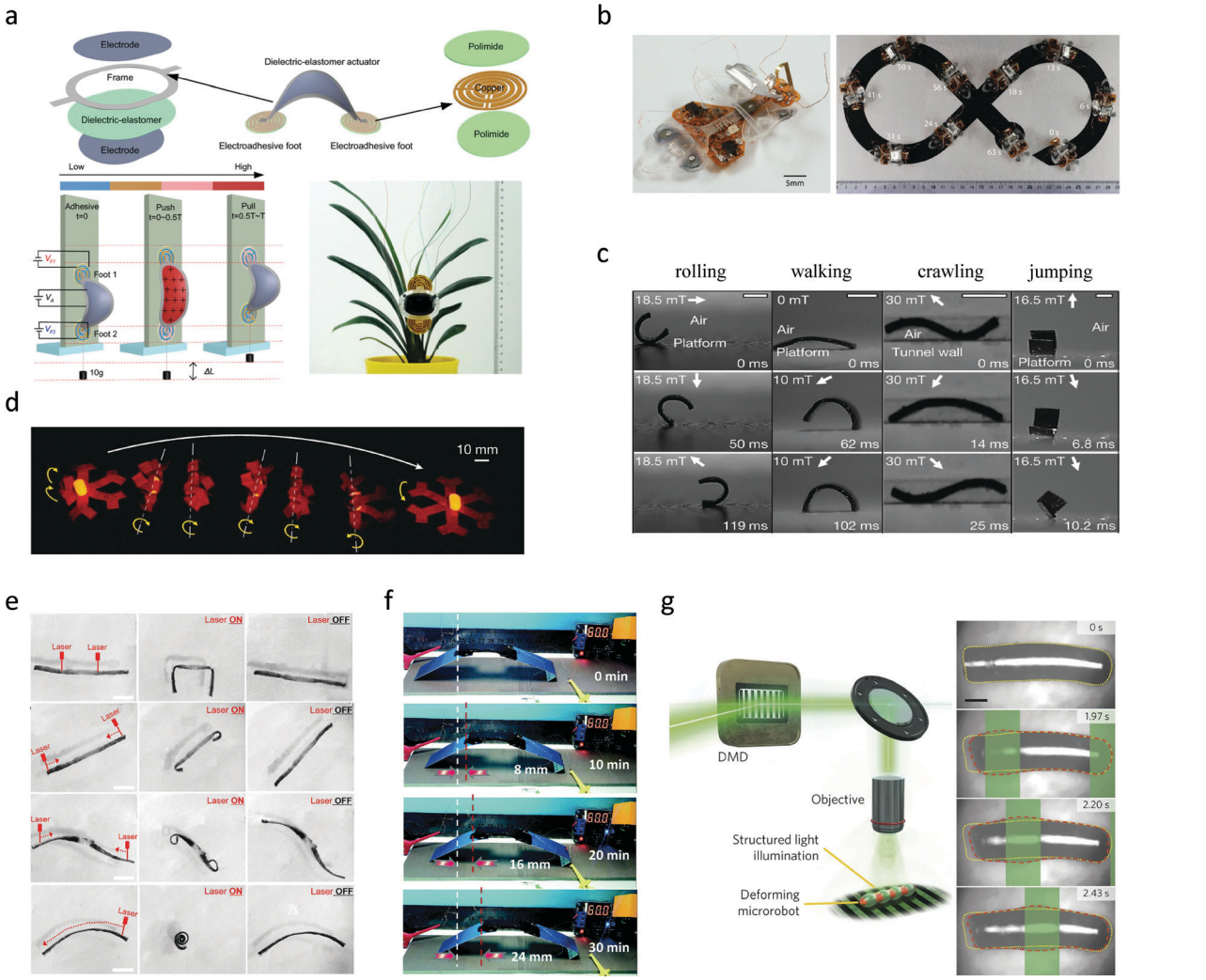

Fig. 7 Locomotion robots based on stimuli-responsive materials. (a) A soft wall-climbing robot with a DEA as the main body and two bipolar electroadhesive pads as the feet, with controlled adhesion. Reproduced with permission.[120] Copyright 2018, AAAS. (b) An autonomous untethered robot driven by low-voltage stacked DEAs. Reproduced with permission.[121] Copyright 2019, AAAS. (c) Some of the locomotion modes of the soft magnetic microrobot. Reproduced with permission.[105] Copyright 2018, Springer Nature. (d) A 3D printed soft magnetic robot wraps a pill and carries it by rolling in response to a rotating magnetic field. Reproduced with permission.[104] Copyright 2018, Springer Nature. (e) Multiple locomotion modes of photo/thermo responsive composite hydrogels under NIR laser stimulation. Reproduced with permission.[127] Copyright 2015, Wiley. (f) A soft inchworm-type locomotive robot based on thermo responsive reversible CNT–SMP composites. Reproduced with permission.[128] Copyright 2016, Royal Society of Chemistry. (g) A soft microrobot driven by photo-responsive LCEs. Reproduced with permission.[129] Copyright 2016, Springer Nature.

The rapid progress of soft grippers has elicited potential applications in robotic fields such as object transport, industrial assembly, healthcare and medical devices. Recent advances regarding stimuli-responsive grippers are reviewed in this section, covering material selection, operation mechanisms and mechanical properties.

Stimuli-responsive material based soft grippers partially or entirely employ these active materials as actuation components. The most classic type of soft grippers is constructed from fluid elastomer actuators (FEAs).[11] Actuation is generated through an external fluid (air or liquid), which is pressurized into chambers composed of passive deformable materials like silicone elastomers. While FEA grippers are widely used due to advantages such as high output force, simple design and mature fabrication, long response time and invariant rigidity result in their limited grasping and manipulation capability. For this reason, researchers have exploited hybrid structures integrating active responsive materials with the architecture of FEAs, which enable tunable stiffness[133] or effective length.[134] As shown in Fig. 8a, thermosensitive SMP layers embedded in pneumatic actuators can tune the stiffness by 120 times with fast response speed, significantly enhancing the adaptability and operating ranges of grippers.[72] Hydrogels can also be implemented to construct hydraulic actuators with high-force and high-speed simultaneously and maintain robustness over long-term tests.[135] However, despite the versatile capability introduced by stimuli-responsive materials, the coordination of multiple actuation components requires further exploration.

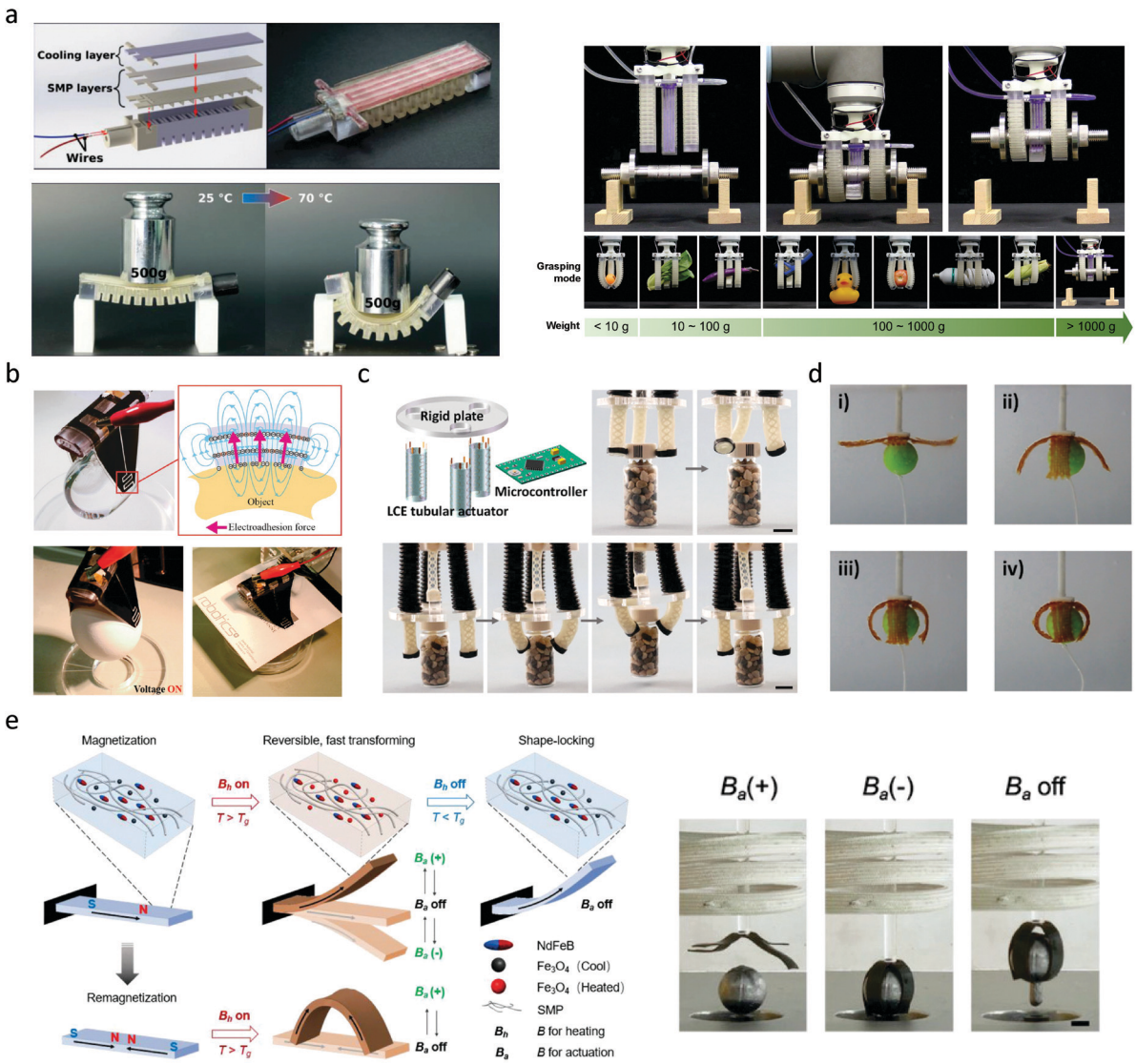

Fig. 8 Soft grippers based on stimuli-responsive materials. (a) A fast-response, stiffness-tunable gripper integrating pneumatic actuators with SMP layers that can maneuver various objects with a wide range of weights, spanning from less than 10 g to 1.5 kg. Reproduced with permission.[72] Copyright 2019, Wiley. (b) An electrostatic actuation based DEA gripper with intrinsic electroadhesion force enabling manipulation of delicate and flat objects. Reproduced with permission.[141] Copyright 2016, Wiley. (c) A compact electrically controlled LCE gripper with capabilities of grasping a vial (50 g) and twisting its cap. Reproduced with permission.[144] Copyright 2019, AAAS. (d) A four-armed gripper constructed by extrusion-based printing of tough hydrogels in response to saline solution (size of each arm: 15 mm × 6 mm, maximum output force: 0.15 N). Reproduced with permission.[145] Copyright 2018, Wiley. (e) A multifunctional lightweight gripper (0.47 g) achieving reversible and shape locking grasping of a lead ball (23 g) through integrating hard magnetic particles with SMPs. Reproduced with permission.[148] Copyright 2020, Wiley.

Another class of soft grippers based on active responsive materials are entirely actuated by external stimuli. One representative actuation means relies on the response of EAPs to electric stimuli like DEAs. The large actuation strain, fast response speed and high electromechanical efficiency make DEA-based grippers advantageous over other types of soft grippers.[8,136] A wide variety of robotic grippers have been demonstrated with diverse configurations of DEs, such as planar,[137] tubular[138] and rolling[139] structures. However, the output force of grippers actuated by DEAs is typically limited due to the large actuation strokes.[11,138] To provide a high holding force, approaches like tunable rigidity[140] and interfacial adhesion[141] can be introduced to enhance the grasping capacity. As shown in Fig. 8b, Shintake *et al.* presented a DEA with patterned compliant electrodes of interdigitated geometry, simultaneously maximizing the electroadhesion force and electrostatic actuation.[141] The resulting lightweight gripper with sufficient shear holding force is capable of handling fragile objects like a raw egg and planar objects like paper. Additionally, since the operating voltage of DEAs ranges on the order of several kilovolts, miniaturization of a high voltage supply and electrical safety are required to achieve widespread practical applications of untethered DEA-based grippers. Other than EAPs, other stimuli-responsive materials such as SMPs,[73] LCEs[142] and hydrogels[143] can also be utilized as main

actuation elements for grippers. For example, a multifunctional LCE-based tubular gripper controlled by a low voltage (1.0 to 3.0 V) has been developed (Fig. 8c).[144] The actuation mode of Joule heating replicates direct environmental heating and thus facilitates the integration of portable and untethered robots. Another study presented a 3D printed tough hydrogel gripper responsive to saline solution as shown in Fig. 8d.[145] The handling force reaches up to 115 times the weight of the gripper while its response speed is limited (60 s for grasping a ball).

Recently, the converging of multiple materials and mechanisms has opened up an opportunity for the creative design of soft grippers. For instance, traditional universal grippers are actuated by passive granular jamming[146] with bulky and complicated external devices. Linghu *et al.* combined a simple shape-programmed SMP with the concept of universal grippers, enabling versatile grasping capability for multiscale, arbitrarily shaped objects.[147] Magnetic particles can also be integrated with LCEs[142] and SMPs[148] to provide grippers with remote control and location guidance. Ze *et al.* reported a multifunctional gripper with reprogrammable, reversible actuation and shape locking, which is comprised of hard magnetic materials (Fe_3O_4 and NdFeB) and SMPs (Fig. 8e).[148] Since the functionalities of soft stimuli-responsive grippers have been demonstrated, future work will concentrate on the exploration of novel mechanisms, the promotion of the overall properties and the establishment of precise control models for grasping.

3.3 Sensors

Stimuli-responsive material based sensors transform detected information such as strain, pressure, and temperature to electronic signals and thus endow soft robotic systems with indispensable bionic perception.[15,55,149] Compared to conventional rigid sensors with mature fabrication methods and robust sensing performances, the emerging technologies regarding soft sensors remain in their infancy. One of the main reasons lies in the hindrance of existing material properties including stretchability, conductivity, and mechanical/electrochemical/thermo stability and the limitation of responsive mechanisms. Among the stimuli-responsive materials categorized in this review, conductive hydrogels have been the most attractive materials applied in the field of soft sensors, since they exhibit excellent conductivity, stretchability, and transparency for various sensing mechanisms (such as resistive, capacitive, and triboelectric) at low voltages. In general, the conductivity of hydrogels is realized through incorporation of free ions, conductive polymers and nanocomposites.[55] For example, Suo and Whitesides proposed a new type of sensory sheet called ionic skin in 2014, which innovatively explored soft strain and pressure sensors based on ionic hydrogels.[54] Prototypes of soft sensors have been developed over the past few years, and recent attention is mainly paid to the enhancement of the sensing properties, diversity of fabrication methods, and multifunctionality of design principles.

Highly stretchable responsive materials can be used for strain sensors and have developed broad applications such as human-motion detection[60] and gesture recognition.[70] A wearable strain sensor composed of a double-network PAAm hydrogel and calcium–alginate microfibers containing PEDOT:PSS exhibits a maximum strain of 300% with a resolution of 0.1%, satisfying the requirements for the strain range of human motions.[63] Apart from the mechanical response capability, it is significant to explore sensing materials capable of working under extreme conditions akin to some properties of natural skins. A PAAm–PVA–MXene–ethylene glycol (EG) composite based strain sensor achieves an antifreezing property (−40 °C), long-term moisture retention and self-healing capability without comprising its excellent sensing performances.[150] Further, to ensure convenience and robustness in practical applications, systematic integration rather than single sensor components has also been investigated. Gu *et al.* reported a fully integrated highly stretchable untethered skin system with multiplex ionic-hydrogel strain sensors and a wireless electronic control module (Fig. 9a).[70]

Artificial skins with pressure-sensing capability are critical for soft robotics to mimic human sensory ability and have elicited various applications including tactile information extraction,[54] physiological signal monitoring[43,151] and touch panel displays.[152,153] Notably, the sensitivity is considered as a crucial criterion for the sensing performances of soft pressure sensors, resulting in numerous studies having concentrated on the enhancement of sensitivity. For example, Pan *et al.* proposed a hollow-sphere microstructure of a polypyrrole hydrogel and elevated the sensitivity of a resistive pressure sensor up to 56.0–133.1 kPa^{-1} in the low-pressure regime.[154] Besides structure design, the exploration of the pressure-sensing mechanism also presents remarkable influences on pressure sensors. The supercapacitive principle can be applied in ionic capacitive pressure sensors and increase the sensitivity compared to the conventional parallel-plate capacitive principle owing to the unique electric double layer capacitance (C_{EDL}) structure.[151,155] Bai *et al.* developed a supercapacitive principle based skin composed of a microstructured PVA/H_3PO_4 hydrogel and Au nanofilms and achieved an unprecedented sensitivity over 220 kPa^{-1} (Fig. 9b).[156] Magnetic sensing mechanisms leveraging the stimuli-response of magnetic materials can also be applied in pressure sensors. Wu *et al.* reported a sensor based on giant magneto-impedance (GMI) materials as the inductive sensing element.[157] When an external force is exerted on the membrane of a polymer magnet, the magnetic field increases and thus the impedance of the GMI materials decreases. As shown in Fig. 9c, the proposed sensor can distinguish the movement of a small live insect of 0.8 mg on the surface.[157] Regarding fabrication methods, a wide variety of studies generally adopt laborious approaches like solvent casting,[70,156] limiting scalable production and industrial versatility. Recently, integrated fabrication techniques such as 3D printing have been exploited to achieve rapid manufacturing and reliable chemical bonding. A dual-material printing strategy has been applied to fabricate ionic skins with long-term stability, which successively prints hydrogels (PAAm/PEGDA/Mg^{2+}) as electrodes and water-dilutable polyurethane acrylate (WPUA) as a dielectric layer (Fig. 9d).[158]

Apart from one-mode soft sensors such as a strain or pressure sensor, multifunctional sensors with multiple detection

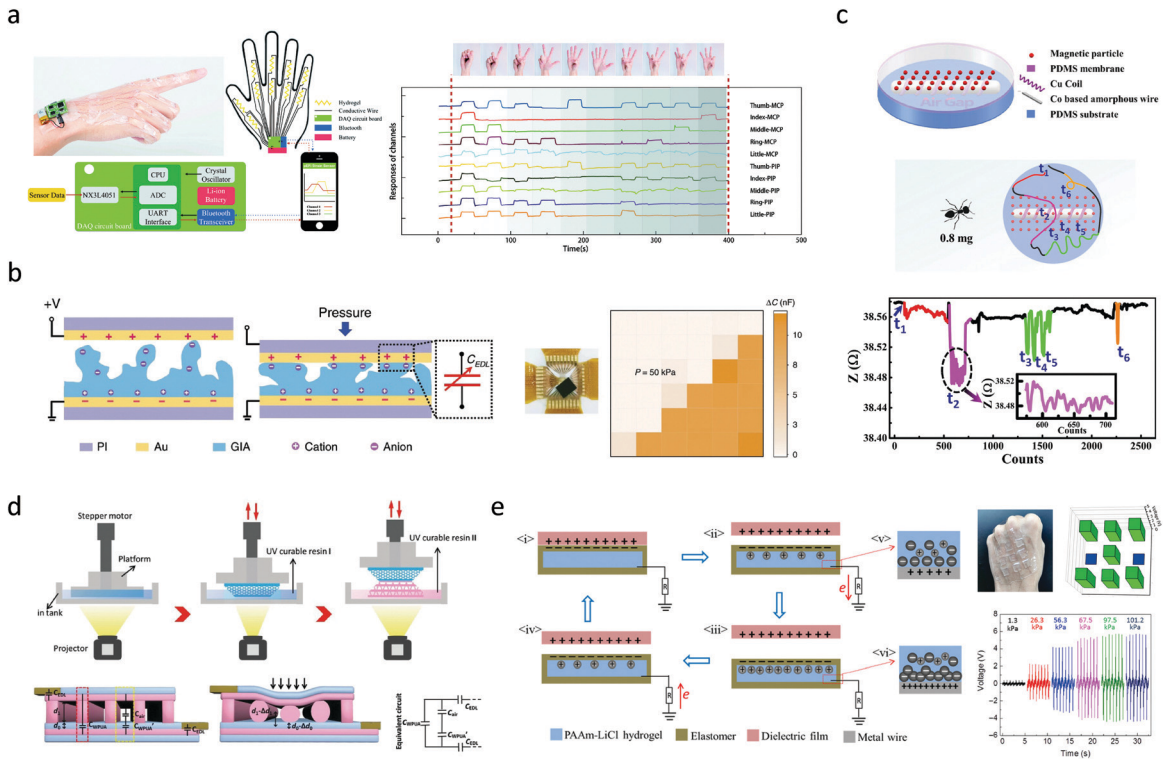

Fig. 9 Soft sensors based on stimuli-responsive materials. (a) A strain-sensing based, fully integrated, transparent PAAm–LiCl hydrogel skin with wireless communication for human-motion monitoring. Reproduced with permission.[70] Copyright 2019, Mary Ann Liebert, Inc. (b) A PVA/H_3PO_4 based, microstructured, supercapacitive pressure sensor with ultrahigh sensitivity (>220 kPa^{-1}), high-pressure resolution (~18 Pa) and high spatial resolution (~100 μm). Reproduced with permission.[156] Copyright 2020, Springer Nature. (c) A magnetic pressure sensor based on GMI materials capable of detecting a moving small ant (0.8 mg). Reproduced with permission.[157] Copyright 2018, AAAS. (d) A dual-material 3D printed ionic skin comprised of a deformable hydrogel-acrylate-based polymer composite with reliable pressure sensing capability in long-term use. Reproduced with permission.[158] Copyright 2019, Wiley. (e) An ionic hydrogel TENG enabling both tactile perception and energy harvesting. Reproduced with permission.[161] Copyright 2017, AAAS.

dimensions hold great potential in integrated robotic systems. For instance, Lei *et al.* developed a supramolecular polyelectrolyte hydrogel based biomimetic skin capable of simultaneously sensing the change of strain, stress and temperature.[159] A bimodal sensory array achieves pressure-sensing and temperature-displaying through a hybrid parallel-plate capacitive structure composed of polyampholyte (PAm) hydrogels as electrodes and a thermochromic liquid crystal (TLC) as dielectric layers.[160] A MXene-hydrogel-based strain sensor exhibits asymmetrical sensitivity under compressive strain and tensile strain, and thus presents the capability of distinguishing the direction and speed of motions on the sensor surface.[60] In addition, Pu *et al.* combined the principle of triboelectric nanogenerators (TENGs) with an ionic-hydrogel sensing mechanism. Their proposed soft skins simultaneously enable energy harvesting and tactile sensing, which exhibit high stretchability (1160%), a peak power density of 35 mW m^{-2} and a limit of detection (LOD) of 1.3 kPa (Fig. 9e).[161] However, existing multifunctional sensors have to overcome the limitations on structure complexity and signal coupling. Next-generation soft sensors will make a great difference in various fields including multi-dimension sensing, synchronous recognition and energy supply.

4. Conclusion and outlook

In this review, we have discussed the latest progress of stimuli-responsive materials toward their applications in soft robotics. Robots and devices in response to multiple external stimuli have opened new scenarios of intelligent machines with locomotion, grasping, and sensing capabilities. The rapid advances of soft robotics are pushing the boundaries confining traditional robotics, which relies on rigid functional components, complicated mechanism designs and cumbersome energy supply devices. Smart soft materials are promising to create next-generation robots capable of performing dexterous manipulations and accurately sensing the ambient environment akin to humans. However, despite the impressive advancement, there remain a number of challenges to be addressed in the future.

Soft stimuli-responsive functional materials generally suffer from limited mechanical strength, hindering their commercial and long-term utilization for robots and devices. Self-healing ability can be introduced to enhance the robustness and adaptability of responsive materials. Nevertheless, self-healing devices mostly remain at a proof-of-concept stage, and further research on healing mechanisms and performances is required. Compared to rigid materials, soft materials also exhibit inferior

repeatability and uniformity with adverse influences. The hysteresis induced by the ubiquitous viscoelasticity of elastomers and gels may result in signal baseline drift of electronic skins and undesired output of soft actuators. Currently, trade-offs among various properties of responsive materials need to be made to realize the optimization of the developed soft robots and devices. Moreover, theoretical research on responsive mechanisms of materials should be explored in depth. For instance, Wang and co-workers recently demonstrated the electro transfer phenomenon in the formation of liquid–solid EDLs, which significantly influenced the traditional understanding of the principle of EDLs.[162,163]

To date, the practical applications developed using existing soft robotic systems based on stimuli-responsive materials are still limited. One of the main concerns is about the relatively low output force of fully soft material based actuators. Akin to many biological bodies supported by a skeleton, it will be an attractive direction to merge soft responsive materials with rigid frameworks in the near future. Functional materials with variable stiffness capability can also benefit the design of stiff–soft duality of actuators. Another challenge is the development of untethered soft robots. To fully eliminate the tether, continuing efforts are required involving on-board electronics, sensing feedback and remote actuation mechanisms. Additionally, the current laboratorial fabrication methods limit the real-world applications of soft robotic devices. Fast, precise and low-cost manufacturing techniques out of the laboratory are necessary to develop commercial soft robotic applications. Although recent advances in terms of individual components like soft actuators and sensors have been reported, integrated robotic systems with desired robustness, industrial viability and user-friendliness are challenging. Portable and miniaturized energy supply devices are required to improve the applicability of soft robotics. The incorporation of energy harvesting mechanisms can also provide feasible solutions to self-powered robotic systems. In addition, the following research should pay more attention to wireless communication, real-time control and signal processing capabilities of flexible circuits, and thus reduce the current dependence on rigid printed circuit boards and external processors. The systematic integration of various components will ultimately propel the translation of soft robotics into practical applications.

The aforementioned challenges elicit interdisciplinary collaboration including chemistry, materials science, mechanical engineering, biology and mathematics. Machine learning and data-driven technologies can also be introduced to enable experience-free, complex designs of architectured materials and systematic configurations. Throughout the future developments, ongoing efforts from researchers aiming to address these challenges are paving the way for next-generation smart materials in soft robotics.

Conflicts of interest

There are no conflicts to declare.

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