ACS Partner Journal
ACCOUNTS
—of materials research—

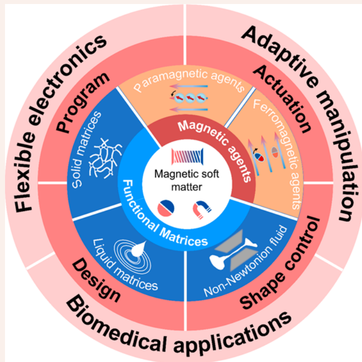
pubs.acs.org/amrcda
Article

Magnetic Soft Matter toward Programmable and Multifunctional Miniature Machines

Neng Xia, Dongdong Jin,* and Li Zhang*

Cite This: *Acc. Mater. Res.* 2024, 5, 173−183
Read Online

CONSPECTUS: Miniature machines that are highly controllable have received widespread attention due to their potential applications in smart medicine and micromanipulation, especially those developed based on soft matter. The inherent compliance of soft matter can enhance the adaptability of miniature machines to a complex working environment or the objects being manipulated. Furthermore, with the rapid development of materials science and control technology, the emergence of various responsive soft matters has promoted the remote and even autonomous actuation capabilities of miniature machines as well as reconfigurable properties. Despite burgeoning efforts devoted to the programming and precise control of soft machines, the exploration of miniature soft machines is still in its infancy. Due to the nonlinearity of the response of active soft matter, a comprehensive understanding of the modeling and control of its deformation and actuation is needed. Besides, systematic study on on-demand programming of material components and physical properties at the submillimeter, micro-, and even nanoscale levels is also important. Hence, more in-depth research on the material composition, response mechanisms, and programming methods of soft matter is needed to promote the construction of novel and practical soft machines in the future.



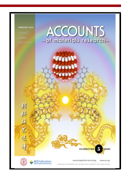
Based on the regulation of various physical fields or chemical substances, active soft matter can demonstrate controllable shape-morphing capabilities without restraint. Among the stimulation methods, the magnetic control strategy possesses outstanding advantages in terms of safety, controllability, and penetration depth, which endow magnetic soft matter with huge potential in fundamental study and engineering applications. Programmable magnetic soft matter provides a powerful platform to explore complex deformation patterns and locomotion behaviors in nature. Under the action of nonuniform magnetic torques generated by programmable magnetic stimulation, magnetic soft matter could undergo a series of reconfigurable morphological transformations. Besides, magnetic soft matter provides a promising solution for developing soft machines with optimized actuation speed and energy density. Therefore, through exquisite assembly and structural design, miniature machines composed of magnetic soft matter are compatible with many application scenarios, especially for biomedical engineering.

In this Account, we provide a comprehensive overview of the recent significant advancements achieved by our group and others in terms of magnetic soft matter. First, we elucidate the interaction mechanism between diverse magnetic agents and actuation magnetic fields as well as various available matrices for magnetic soft machines, including polymer matrices, liquid matrices, and non-Newtonian fluids. We then illustrate the programming methods for encoding heterogeneous magnetization profile or magnetic particle orientation, as well as the development of 3D morphological transformations under magnetic stimulation (e.g., origami or kirigami deformation, surface with nonuniform Gaussian curvature). Next, the potential applications of magnetic soft machines are discussed, focusing on recent advancements in micromanipulation, biomedical devices, and flexible electronics. Finally, we provide an outlook on the prospects and opportunities for the future development of magnetic soft machines to promote their practical applications.

1. INTRODUCTION

Reconfigurable soft machines are a class of flexible devices or robots with active control capability as well as inherent compliance, and promise enormous benefits in the applications of medical treatment, industrial detection, and micromanipulation.[1−3] Exploring the adaptability and multifunctionality of miniature soft machines has been a hot topic in the academic community. First, the capability of adapting to complex and changeable physical environments and chemical cues enables soft machines to complete challenging tasks.[4,5] In this regard, burgeoning efforts to develop responsive and programmable machines are emerging.[6,7] Second, endowing soft machines with multifunctionality could improve the efficiency of task execution and expand application scenarios, while it requires

Received: November 1, 2023
Revised: December 14, 2023
Accepted: December 21, 2023
Published: January 22, 2024



https://doi.org/10.1021/accountsmr.3c00227
Acc. Mater. Res. 2024, 5, 173−183

the ability to seamlessly integrate multiple heterogeneous units.[8−10]

A comprehensive understanding of the functional components, programming strategies, and shape control mechanisms of soft matter is important for developing the next generation of smart soft machines. Depending on the type of actuation source, stimulus-responsive soft matter can exhibit responsive behavior to a range of physical fields and chemical substances (Table S1).[11−16] Light-driven soft machines possess good spatial selectivity and sequential actuation capabilities. However, their tissue penetration depth is limited, making them primarily suitable for actuation in superficial regions of the epidermis. The acoustic actuation method offers excellent biocompatibility and generates substantial driving force and locomotion speed, albeit with limited directionality. Electric field-driven soft machines demonstrate rapid response speeds, but their biomedical applications remain constrained. Soft machines propelled by chemical energy typically exhibit swift movement and high energy density, yet their swimming directionality is compromised. Moreover, the presence of chemical fuels necessitates the consideration of potential toxicity. Among the various types of active soft matter, magnetic soft matter has attracted great interest due to its programmability and response speed.[17−20] Another feature different from other types of active soft matter is the diversity of forms of magnetic soft matter, including solids, liquids, and non-Newtonian fluids.[21,22]

This Account highlights the recent advancements in miniature soft machines based on magnetic soft matter, especially the progress made by our group over the past 5 years. First, we illustrate the interaction between magnetic soft matter (consisting of magnetic agents and soft matrix) and magnetic fields. The programming methods of magnetic soft matter and reconfigurable morphological transformations are discussed. In addition, we present various engineering applications of magnetic soft machines. Finally, we present our perspectives on future development opportunities.

2. KEY COMPONENTS OF MAGNETIC SOFT MATTER

2.1. Properties and Responsive Behaviors of Magnetic Agents

2.1.1. Paramagnetic/Superparamagnetic Agents. Magnetic materials can be divided into diamagnetic, paramagnetic, and ferromagnetic materials according to their magnetic susceptibility (χ). Paramagnetism is a weak effect, as paramagnetic agents exhibit weak attraction to magnetic fields. Since $\chi > 0$, the direction of magnetization $\boldsymbol{M}$ will be parallel to the direction of $\boldsymbol{H}$ (the field generated by free current, $\boldsymbol{H} = \boldsymbol{M}/\chi$), and when the external magnetic field is removed, the magnetization will drop to 0. Superparamagnetic agents are a special type of material with no coercive force and residual magnetization, but with high magnetic susceptibility (Figure 1a).[23,24]

When paramagnetic agents are dispersed within a polymer matrix or a liquid environment, they can undergo structural deformation, including stretching and bending, in response to magnetic force (indicated by eq 1) or magnetic torque (indicated by eqs 2 and 3).[7,25]

$$\boldsymbol{F} = \nabla \boldsymbol{B} \cdot \boldsymbol{M} \tag{1}$$

$$\boldsymbol{\tau}_{m1} = N \frac{4\mu_0 n^2 \chi^2 R^6 \pi}{3d^3} \boldsymbol{H}^2 \sin 2\alpha \tag{2}$$

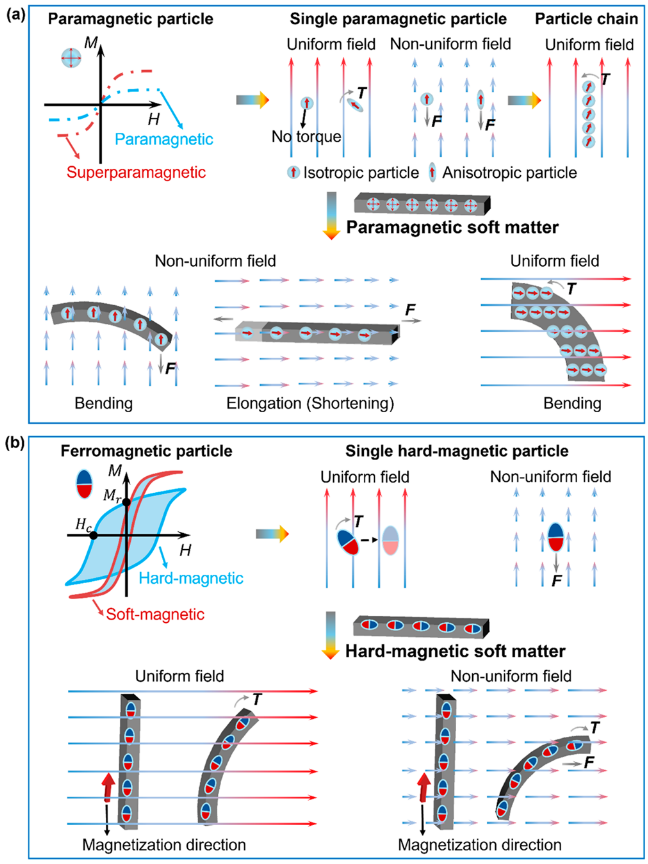


Figure 1. Classification and responsive behavior of magnetic agents. (a) Paramagnetic agents. Paramagnetic and superparamagnetic particles have no coercivity and no remanence. (b) Ferromagnetic agents. Ferromagnetic particles include soft and hard magnetic particles. Soft magnetic particles exhibit a narrow hysteresis curve, while hard magnetic particles have strong coercive force and remanence.

$$\boldsymbol{\tau}_{m2} = \boldsymbol{M} \times \boldsymbol{B} \tag{3}$$

$\boldsymbol{F}$ and $\boldsymbol{\tau}_{m1}$ ($\boldsymbol{\tau}_{m2}$) are the magnetic force and torque, respectively. $\nabla \boldsymbol{B}$ represents the gradient of the magnetic field. $\boldsymbol{M}$ is the magnetic potential of the magnetic material. n and N are the number of paramagnetic particles in a chain and the number of paramagnetic chains in the structure, respectively. μ_0 and χ are the vacuum permeability and magnetic volume susceptibility of paramagnetic particles, respectively. R is the diameter of paramagnetic particle. d represents the interparticle distance. $\boldsymbol{H}$ is the magnetic field intensity. α is the angle between the particle chain and the external magnetic field. $\boldsymbol{B}$ represents the external magnetic field.

By introducing magnetic anisotropy (such as shape-anisotropic particles), the symmetry of its response can be broken and a magnetic torque can be formed.[26] In addition, the formation of anisotropic particle chains has been widely explored to achieve complex torque-driven deformation.[7] These immobilized chains of paramagnetic particles within the polymer matrix generate magnetic dipole interaction induced torque when subjected to the external magnetic field, resulting in programmable structural deformation.

2.1.2. Ferromagnetic Agents. The magnetization intensity of ferromagnetic agents is highly nonlinear and is usually expressed in the form of a hysteresis loop. According to the intensity of the coercive force, it can be divided into soft-magnetic and hard-magnetic materials. Soft-magnetic materials belong to a category of magnetic materials that are distinguished by their low remanence and coercive force, along with their high magnetic susceptibility and saturation magnetization (Figure 1b). Examples of soft magnetic materials typically encompass soft ferrite, iron−silicon alloy, iron−nickel alloy, and others.[7,27,28] In the absence of an external magnetic field, soft magnetic materials are unable to retain strong remanence and are susceptible to remagnetization when exposed to an external field. The magnetostrictive behavior of soft magnetic particles could also lead to the deformation of the polymer matrix when subjected to a high-intensity magnetic field. This behavior finds wide applications in artificial muscles and vibration isolation system.[29,30]

In contrast to soft magnetic materials, hard magnetic materials possess high coercive force and remanence (Figure 1b).[16,31] By incorporating hard magnetic materials into soft polymer matrices, the resulting composites can undergo structural deformation under magnetic torque (as indicated by eq 3). The deformation mode of these composites is determined by the regulation of the magnetic domain pattern within the hard magnetic materials. Under a nonuniform magnetic field, ferromagnetic materials can be attracted by force and torque at the same time, resulting in increasing deformation.

2.2. Classification and Properties of Functional Matrices

Before introducing soft matrices, we first categorize the interaction between magnetic agents and different matrices into three types, i.e., surface interaction, embedment, and dispersion (Figure 2a). With the help of surface interaction forces such as electrostatic force or dielectrophoresis, magnetic particles can be distributed on the surface of the matrix material.[32,33] In addition, Dong et al. employed a tape network to bond and transfer magnetic particles, which are stably embedded within the tape's adhesive layer.[9] The most common approach for developing magnetic soft materials is to disperse magnetic units directly into the matrix. In cross-linked polymer networks, the orientation of magnetic particles is difficult to change.[34,35]

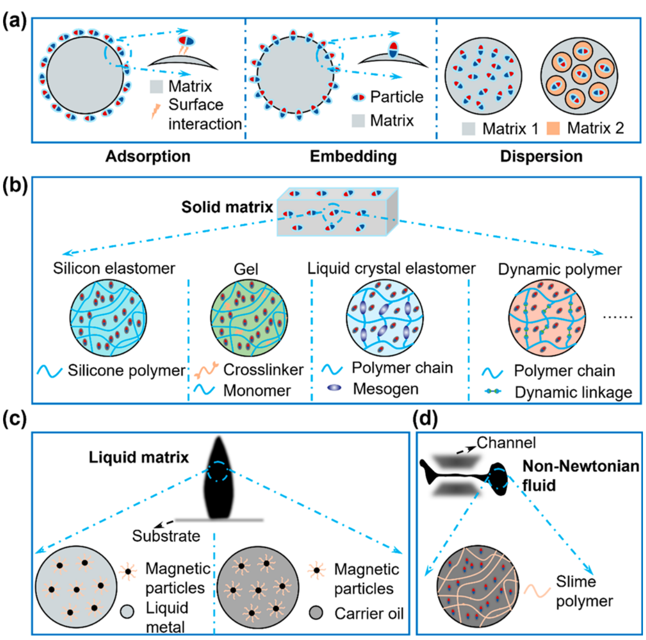


Figure 2. Classification of flexible matrices for magnetic soft matters. (a) Interaction between magnetic particles and matrices. (b) Solid matrices including silicone elastomer, gel, liquid crystal elastomer, dynamic polymer, and other types of polymers. (c) Liquid matrices based on liquid metal or carrier oil. (d) Non-Newtonian fluid.

Establishing a robust connection between the magnetic agent and the matrix is a crucial factor in guaranteeing the reliability of magnetic soft machines. The bonding ability between them can be assessed using techniques such as an atomic force microscope or adhesive materials such as tape. Depending on the matrix material and working environment, causes of the failure of interfacial interactions include mechanical exfoliation, corrosion (especially in aqueous environments), alloying reactions, and surface energy mismatch. To address potential failures, the chemical modification of magnetic agents is crucial. This can involve grafting polymers with abundant double bonds onto the magnetic particle surface to create cross-linking sites for connecting the particles and the matrix. Additionally, coating the magnetic particles with a thin layer of SiO_2 can prevent corrosion, while employing Ag nanoparticles can functionalize the particle surface and adjust its wettability with liquid matrices.[36]

The preparation methods for magnetic soft machines can be categorized into mold-assisted methods, additive manufacturing methods, self-assembly, and manual assembly methods. Among these, the mold-assisted method is widely utilized. This approach involves filling the mold with a mixture of a polymer precursor and magnetic agents. This strategy is user-friendly, as it requires minimal specifications for the polymer precursor's properties, making it suitable for creating simple geometric shapes. The advancement of diverse 3D printing technologies, including two-photon polymerization (TPP), direct ink writing (DIW), and digital light processing (DLP), offers significant strategies for constructing magnetic soft machines with intricate shapes and programming their physical intelligence. When it comes to manufacturing precision, the TPP method excels in processing complex magnetic structures with submicrometer resolution, such as spiral structures and burr-like porous spheres. The DIW strategy demonstrates exceptional capabilities in multimaterial molding and enables seamless integration of multiple modules or the construction of multistimulus-responsive structures in magnetic soft machines. On the other hand, the DLP strategy allows for rapid construction of 3D structures through layer-by-layer photo-cross-linking, while also facilitating in situ programming of magnetic domains through external field control. In contrast, self-assembly and manual assembly methods offer the potential to overcome the limitations in structure, material, and magnetic domain orientation present in other fabrication techniques. These methods enable the creation of magnetic soft machines with arbitrarily complex structures, material components, and 3D magnetic domain distributions. However, it is important to consider the stability of the interface connection and the complexity of the assembly process when using these methods.

Based on the existence form, different matrices are categorized into solid, liquid, and non-Newtonian fluid.[37,38]

2.2.1. Solid Matrices. Silicone rubber, including polydimethylsiloxane and Ecoflex, is widely favored for the study of soft robotics due to its desirable elastic modulus and toughness.[39] The composition of magnetic particles and uncured silicone rubber can be shaped through molding or

https://doi.org/10.1021/accountsmr.3c00227
Acc. Mater. Res. 2024, 5, 173−183

ink printing.[16] Thermoplastic polymers, such as thermoplastic polyurethanes, can undergo melt-reprocessing and possess good mechanical properties such as strength and toughness.[27] However, compared to silicone-based elastomers, their higher modulus makes them more suitable for situations with low structural stiffness or actuation fields with high intensity.

The incorporation of responsive polymers allows both the matrix and magnetic units to actively react to external stimuli, thereby promising enhancement of the functionality of magnetic soft machines. One class of responsive polymers used in magnetic soft materials are hydrogel materials, which are 3D cross-linked networks consisting of hydrophilic polymers and are known for their softer properties and lower modulus, primarily attributed to their large water content.[40,41] Depending on the type of stimulus, hydrogels that respond to pH, temperature or light have been widely developed and employed in magnetic soft robots.[38] The responsive behavior of these hydrogels arises from the protonation or deprotonation of ionizable side groups, which further induces electrostatic repulsion between polymer chains. Another commonly adopted responsive polymer is liquid crystal elastomers. The polymer network contains anisotropic mesogenic units. The reversible deformation of the elastomers is triggered by the order−disorder transition of the mesogens under external stimulation. To enhance the reprogrammability of magnetic soft robots, significant advancements in the development of dynamic polymer networks have been made. These networks possess the ability to form stable interface bonding under external stimulation or spontaneously, and can even be fully recycled and repolymerized to form a new magnetic robot structure.[42]

2.2.2. Liquid Matrices. Soft machines utilizing liquid media, such as liquid metal or ferrofluid, possess dramatic deformation capabilities.[43,44] Ferrofluids are stable colloidal suspensions consisting of magnetic nanoparticles, carrier fluid, and surfactant.[43] When subjected to an external magnetic field, ferrofluids exhibit a variety of deformation behaviors, including stretching, fission, and fusion. Additionally, they can also demonstrate locomotion behaviors, including rotation and jumping. Moreover, ferrofluids offer the potential to serve as active skin, enabling nonresponsive materials to become actuated.[21] Another liquid carrier commonly employed is liquid metal. For example, by dispersing magnetic particles within phase-changeable gallium, the fluidic machine can undergo a transition between liquid and solid states by adjusting the temperature.[44]

2.2.3. Non-Newtonian Fluid. Liquid matrices based magnetic soft machines often impose specific operating environment requirements. For instance, oil-based ferrofluids need to be manipulated in a water-based environment. In this respect, slime robots based on non-Newtonian fluids have emerged as a promising solution. These robots not only have the ability to pass through narrow channels but also exhibit mobility on two-phase fluids. This magnetic slime material is comprised of ferromagnetic particles, borax, and poly(vinyl alcohol).[22] It is capable of actively changing its shape when stimulated by an external magnetic field, enabling it to grasp or envelop cargo. Furthermore, due to its sufficient mobility, the hydrogen bonds between groups can be rapidly restored, allowing for self-healing capabilities in robotic applications.

Based on the material properties of the matrices used, current magnetic soft machines exhibit certain limitations that require further improvement (Table S2). First, magnetic soft materials utilizing solid matrices often encounter limitations in terms of reconfigurability, necessitating the incorporation of phase-change materials to confer reprogramming capabilities. The degradation and recycling of soft machines composed of solid polymers continue to pose challenges. Moreover, in comparison to the significant volume changes observed in chemically or light-driven soft materials, magnetic soft machines composed of solid matrices exhibit relatively weaker deformation abilities. Second, magnetic soft machines utilizing liquid matrices impose stringent demands on the working environment, while ensuring the biocompatibility of such liquid soft machines remains a significant challenge. For instance, although an amalgam is a frequently employed liquid metal, its toxicity necessitates researchers to seek alternative materials. Third, for a more comprehensive investigation of future non-Newtonian fluid-based soft machines, their performance enhancement should take into account factors such as output force, long-term stability, and degradability. Due to the 3D porous network that makes up the microstructure of non-Newtonian fluid-based soft machines, the magnetic agents within them are susceptible to corrosion when exposed to liquid environments. In order to effectively address biomedical applications, it is crucial to enhance the complete degradation or safe retrieval capabilities of these non-Newtonian fluid-based soft machines.

3. PROGRAMMABLE SHAPE CONTROL OF MAGNETIC SOFT MATTER

3.1. Bending Deformation of Magnetic Soft Matter

Under the action of distributed magnetic torque, magnetic soft materials are capable of demonstrating various reconfigurable surfaces crossing different scales.[45] First, bending deformation serves as a fundamental building block that contributes to complex shape morphing results (Figure 3a).[46] Ferromagnetic soft materials with the heterogeneous arrangement of continuous or discrete magnetization profiles promise the capability to achieve bending or torsion deformations.[34] The existing programming methods for magnetization patterns can be divided into two categories: the global magnetization method and the voxel-by-voxel regulation method. First, a template-assisted magnetization method developed by Sitti et al. is a straightforward and convenient approach for achieving desired global magnetization in one step (Figure 4a).[37,47] The temporary shape of the magnetic soft material is determined by a template and subsequently experiences a pulsed magnetic field to form heterogeneous magnetization profile. In contrast, the voxel-by-voxel magnetization methods demonstrate the high design freedom of magnetic domains. The methods are often combined with additive manufacturing techniques, such as DIW, DLP, or TPP, during which, the orientation of magnetic particles is dynamically adjusted using permanent magnets or electromagnetic coils (Figure 4c−4d).[24,45,46,48,49] The magnetization methods enable the programming of 3D discrete magnetic domains but are relatively cumbersome and require custom devices.

Natural organisms can exhibit more refined buckling patterns, promoting the dynamic regulation of surface morphology. Furthermore, complex cooperative transformations of cellular lattices have been widely explored in the field of metamaterials (Figure 3a-ii). In this respect, Xia et al. proposed a global magnetization method using the active deformation of magnetic materials.[39] As illustrated in Figure

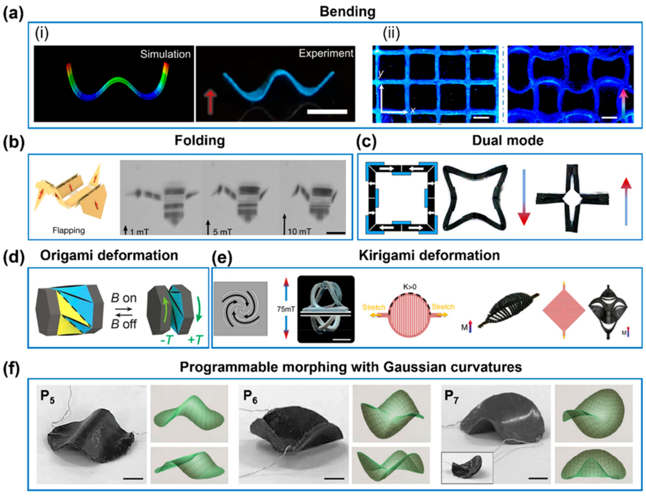


Figure 3. Programmable shape morphing of magnetic soft matters. (a-i) Bending deformation and simulation of a magnetic film. Reproduced with permission from ref 34. Copyright 2020 Springer Nature. (a-ii) Morphological transformation of square lattice with buckling encoded magnetization. Reproduced with permission from ref 39. Copyright 2022 Springer Nature. (b) Folding behavior of a microscale "bird". Reproduced with permission from ref 31. Copyright 2019 Springer Nature. (c) Dual-mode deformation based on asymmetric joints. Reproduced with permission from ref 50. Copyright 2019 American Chemical Society. (d) Folding and unfolding behavior of an active origami structure. Reproduced with permission from ref 52. Copyright 2022 Springer Nature. (e) Active kirigami structure with 3D helical pattern, ellipsoid shape, and 3D face-like shape. Reproduced with permission from ref 53. Copyright 2021 Wiley-VCH. Reproduced with permission from ref 54. Copyright 2022 Wiley-VCH. (f) Curved surfaces with nonuniform Gaussian curvatures. Reproduced with permission from ref 35. Copyright 2020 American Chemical Society.

4b, when the magnetic elastomer absorbs organic solvent, it experiences volumetric swelling and generates buckling transformation under the influence of a bottom constraint. Subsequently, the actively deformed magnetic elastomer is magnetized by applying a pulsed magnetic field, thereby encoding 3D magnetic domains within the soft material. The buckling encoded magnetization offers a template-free method for the rapid formation of heterogeneous magnetization.

3.2. Folding Deformation and Dual Mode of Magnetic Soft Matter

The folding mode of magnetic materials utilizes localized bending deformation to transform a 2D structure with predesigned crease into a 3D shape and is widely employed in origami and kirigami structures (Figure 3b).[31] When programming the internal magnetic domains using the methods in section 3.1, the design of creases in magnetic soft matter promises benefits in reducing the structural stiffness and increasing the deformation amplitude. For instance, Cui et al. utilized silicon nitride membrane to fabricate a microscale bird with hinge spring layouts.[31] Actuated by nanomagnets on the membrane, the microbird can flap a pair of wings with folding behavior. To enhance the actuation mode of magnetic soft materials, Wu et al. proposed asymmetric joints (Figure 3c).[50] By introducing small gaps, the adjacent magnetic cell structures can be actuated by magnetic fields in different directions, resulting in rigid body rotation or elastic deformation and leading to two distinct morphological transformations.

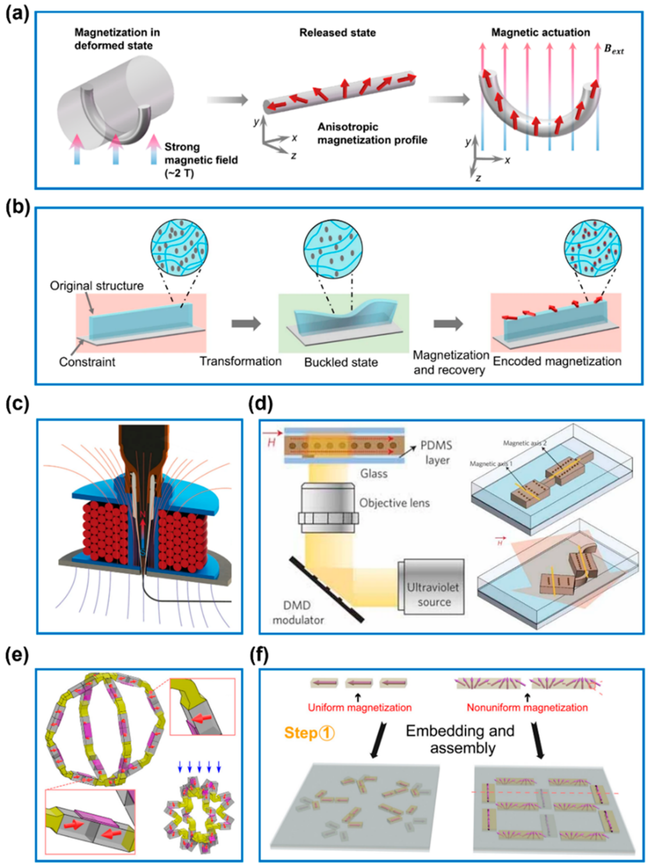


Figure 4. Programming strategies for magnetic soft matters. (a) Template-assisted magnetization strategy. Reproduced with permission from ref 47. Copyright 2022 Wiley-VCH. (b) Buckling instability encoded magnetization. Reproduced with permission from ref 39. Copyright 2022 Springer Nature. (c) Direct ink writing with magnetization programming. Reproduced with permission from ref 48. Copyright 2018 Springer Nature. (d) Digital light processing with magnetization programming. Reproduced with permission from ref 46. Copyright 2019 American Academy for the Advancement of Science. (e) Bottom-up microassembly of heterogeneous micro-building blocks. Reproduced with permission from ref 8. Copyright 2021 American Academy for the Advancement of Science. (f) Programmable magnetization based on tape network. Reproduced with permission from ref 9. Copyright 2022 American Academy for the Advancement of Science.

3.3. Origami and Kirigami Inspired Deformation of Magnetic Soft Matter

Origami and kirigami designs provide rich inspiration for developing magnetic soft machines with complex deformation patterns and promise benefits in bringing about unusual physical properties (Figure 3d−3e). For instance, a magnetic structure that replicates the Kresling origami pattern developed by Ze et al., where two magnetic disks rotate relative to each other under external magnetic field, causing the structure to contract in the length direction while maintaining its width.[51,52] The utilization of cut to guide and enhance out-of-plane deformation of magnetic soft machines has garnered great attention due to their remarkable deformation capabilities. Zhao et al. demonstrated a 3D helical magnetic structure with bistable behavior deriving from a planar structure with four helical cuts.[53] To develop complicated 2D-to-3D shape morphing, Zhu et al. proposed a method that integrates mechanical buckling and magnetic regulation.[54] 3D kirigami structures were obtained by mechanical assembly and then magnetized using pulsed magnetic fields to achieve 3D continuous magnetization profiles. After magnetization, these planar structures can be actuated by magnetic stimulation, enabling the construction of ellipsoid shapes and intricate facial structures.

Bottom-up assembly strategies demonstrate unique advantages in the construction of 3D origami/kirigami structures with programmable magnetic domains.[8,9] As shown in Figure 4e, Zhang et al. used jigs to assist in the assembly of microbuilding blocks under a microscope, and specific faces and edges in the 3D structure were connected by a bonding agent.[8] Taking a cage structure with heterogeneous materials and magnetization patterns as an example, it can shrink along the radial direction under an external magnetic field and exhibit a negative Poisson's ratio. This manual microassembly method has a high degree of freedom but requires a lot of manufacturing time. Recently, our group proposed a strategy to modularly assemble heterogeneous building blocks using adhesive sticker (Figure 4f).[9] The magnetized voxels are directly embedded into adhesive stickers, which avoids additional connection steps and facilitates the seamless integration of other functional modules such as microelectronics.

3.4. Curved Surface with Nonuniform Gaussian Curvature

The development of a 3D surface with programmed Gaussian curvature holds great potential in the fields of flexible electronics, artificial tissues, and soft robotics. However, achieving such sophisticated transformations for complex curved surfaces in magnetic soft matter remains challenging due to the need to encode targeted 3D magnetic domains. At the centimeter scale, the magnetization of these magnetic soft matter can be assisted depending on the design of the mold. As shown in Figure 3f, Song et al. used molds with nonuniform Gaussian curvature to perform the programming of magnetic domains and achieve target transformations.[35] Due to the complexity of 3D surfaces, the design of suitable molds and the magnetization process become difficult at submillimeter and micron scales. Hence, the programming of 3D magnetic domains in miniature magnetic soft matter toward a curved surface is an important research direction.

4. POTENTIAL APPLICATIONS OF MAGNETIC SOFT MATTER

4.1. Adaptive Manipulation Using Miniature Magnetic Soft Machines

The precise manipulation of small-scale objects shows promising prospects in biochemical analysis and microassembly.[55] With the advancements in microfabrication technology, the precise manipulation of micro-objects has become achievable. For instance, Xin et al. developed a TPP-printed magnetic microcrab using pH-responsive hydrogel (Figure 5a).[6] The hydrogel structure was immersed in a suspension of Fe_3O_4 nanoparticles to absorb the magnetic agents. In a liquid environment with a low pH value, the hydrogel network contracts, causing the pincer structure to close and enabling it to grasp a 10 μm × 10 μm SiO_2 bead. Subsequently, the hydrogel micromachine can be guided to target location using permanent magnets for precise delivery.

Based on the interaction between magnetic machines and manipulation objects, multiple manipulation mechanisms have been unveiled including physical contact based on single agent

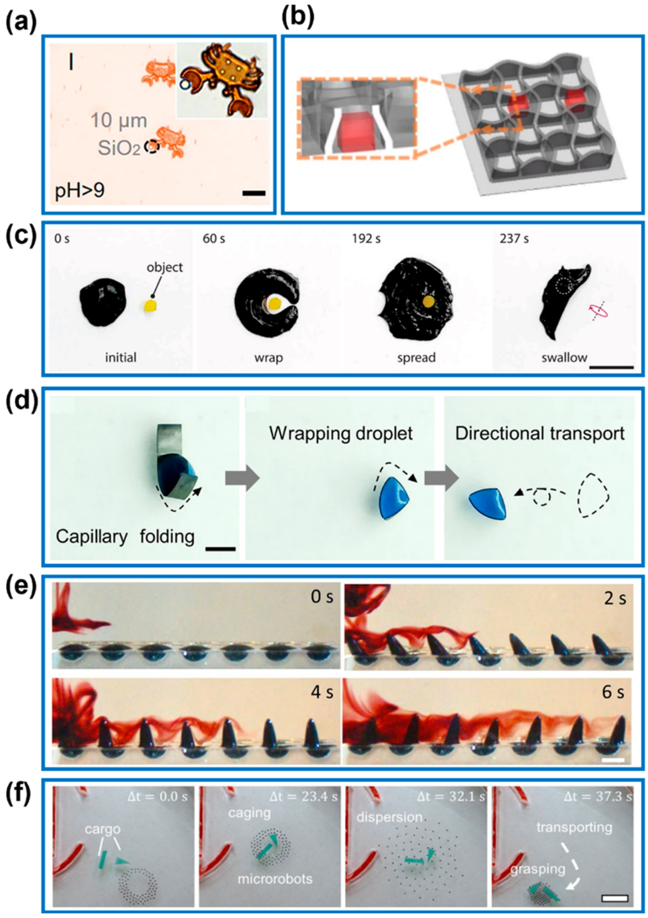


Figure 5. Adaptive manipulation using magnetic miniature soft machines. (a) Tight gripping of a microparticle (10 μm) via magnetic shape-morphing microcrab. Reproduced with permission from ref 6. Copyright 2021 American Chemical Society. (b) Selective particle trapping using magnetic lattice structure. Reproduced with permission from ref 39. Copyright 2022 Springer Nature. (c) The grasp and transport of target objects via the endocytosis of slime robot. Reproduced with permission from ref 22. Copyright 2022 Wiley-VCH. (d) The wrap and transport of droplet by magnetic origami robot. Reproduced with permission from ref 55. Copyright 2023 Springer Nature. (e) The directional pumping of red food dye via a liquid cilia matrix. Reproduced with permission from ref 21. Copyright 2022 Springer Nature. (f) Coordinated control of multiple magnetic robots to manipulate objects. Reproduced with permission from ref 56. Copyright 2020 SAGE Publications.

or group collaboration as well as fluidic interaction. Direct contact is an intuitive method of cargo manipulation, where magnetic machines are often designed in the form of cages or grippers. Adapting to the shape and size of objects for selective or independent manipulation can improve the accuracy and efficiency of task execution. Xia et al. proposed a magnetic microcellular structure encoded by a wavy form magnetization profile, which allows the selective trapping of microparticles by adjusting the size of deformed chambers via magnetic stimulation (Figure 5b).[39] Unlike soft machines made of cross-linked polymers, Sun et al. provide a slime manipulator without fixed shape that can adapt to different cargoes.[22] Attributed to the deformation capability of the non-Newtonian fluid, the slime manipulator could curl, wrap, and swallow various target objects (Figure 5c).

The versatile manipulation of droplets holds significant application value in the study of bioanalysis and chemical reaction. Using capillary or hydrodynamic interactions, magnetic soft machines exhibit unique advantages in droplet manipulation. As shown in Figure 5d, Jiang et al. proposed a Janus magnetic origami robot that can envelop droplets based on capillary force.[55] Under active control, the magnetic robot is capable of performing multiple tasks, including transportation, merging, and splitting. In addition, hydrodynamic interactions provide a noncontact solution for fluidic manipulation. For example, by mimicking the oscillations of ciliary arrays or the gait of jellyfish, magnetic soft machines have been demonstrated to be able to efficiently manipulate liquids and achieve directional transport (Figure 5e).[21]

Cooperative operations between multiple machines promise benefits in enhancing the manipulation capabilities of individual machines. For instance, Dong et al. demonstrated that a robotic swarm consisting of 82 magnetic microrobots spread, contracted, captured, and transferred cargoes under the control of external magnetic fields (Figure 5f).[56] The collaborative manipulation of multiple robots enables them to control objects much larger than those of a single robot.

4.2. Reconfigurable Electronics and Flexible Sensors Based on Magnetic Soft Matters

The reconfigurability of magnetic soft machines has attracted increasing attention because of their promising applications in environmental monitoring, flexible sensing, digital logic computing, and wearable devices (Figure 6a). To realize this application, the integration between magnetic structures and electronic components needs to be considered. For centimeter-scale magnetic soft machines, electronic components can be deployed directly through adhesive agents or printing techniques (Figure 6b, 6c).[51,57] As a typical demonstration of multifunctional modular robots, Dong et al. integrated radio frequency identifier (RFID) tags and magnetic actuation modules into a tape network to detect circuit faults in narrow channels (Figure 6d).[9] 3D printing technologies, especially multimaterial printing, provide a powerful solution for building flexible electronic devices, as they could arrange magnetic units and conductive units in an on-demand manner. Zhao et al. utilized DIW printing to fabricate a soft electronic device that could form different circuitries through dual-modes of shape morphing under magnetic stimulation (Figure 6e).[48] Apart from silver ink, liquid metal, known for its excellent conductivity, finds extensive use in flexible electronics (Figure 6f).[44] Zhang et al. proposed a coaxial printing strategy that involves the simultaneous printing of liquid metal and magnetic elastomer (Figure 6g).[58] In this approach, liquid metal serves as the core unit of the extruded fiber filaments, while a magnetic elastomer acts as the outer active sheath. By monitoring changes in fiber resistance, the integration of sensing and actuation in magnetic soft machines can be achieved.

In recent years, tactile and motion sensing based on monitoring the flux density of magnetic soft materials has attracted widespread attention. As shown in Figure 6h, Hall sensors were utilized to detect the variation of magnetic flux density resulting from the passive deformation of magnetized elastomers.[59] This flexible tactile sensor enables the monitoring of both the magnitude and direction of contact force, making it suitable for human-robot interaction. Zhou et al. presented a novel giant magnetoelastic effect and showcased its applications in implantable power generation devices and human pulse monitoring (Figure 6i).[60] Passive deformation of porous magnetoelastomers leads to alterations in the distribution of surface magnetic flux density. By integration of liquid metal coils onto the surface of the soft patch, changes in magnetic flux density could result in the generation of induced currents.

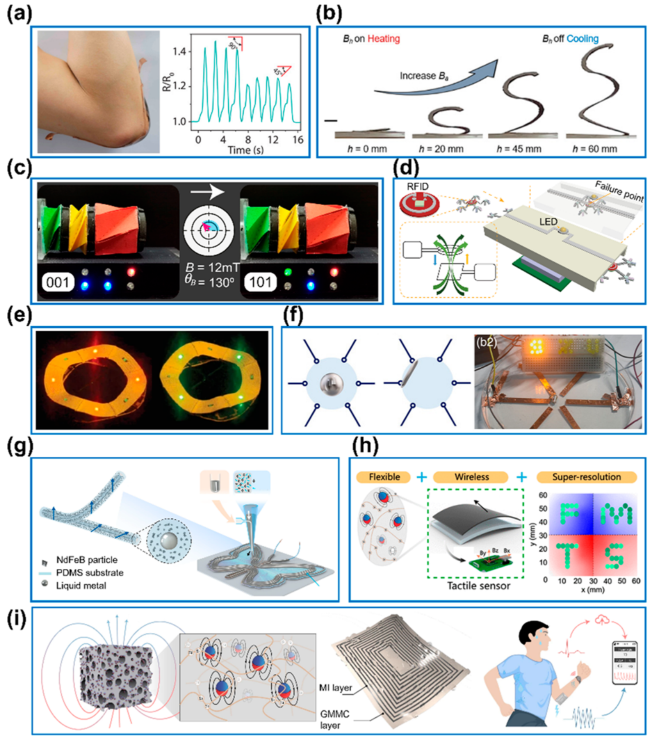


Figure 6. Reconfigurable electronics and flexible sensors based on magnetic soft matters. (a) The bending behavior of elbow was monitored through resistance changes in a tape encapsulated with conductive magnetic slime. Reproduced with permission from ref 22. Copyright 2022 Wiley-VCH. (b) Magnetic shape memory polymers coated with a silver layer were used as reconfigurable antennas. Reproduced with permission from ref 57. Copyright 2020 Wiley-VCH. (c) Magnetic origami structures with bistable property were used in logic circuits. Reproduced with permission from ref 51. Copyright 2020 National Academy of Sciences. (d) A magnetic soft machine integrated with RFID tag was used to detect fault point. Reproduced with permission from ref 9. Copyright 2022 American Academy for the Advancement of Science. (e) A reconfigurable soft electronic device based on the annular ring structure. Reproduced with permission from ref 48. Copyright 2018 Springer Nature. (f) The welding of circuit using magnetic liquid metal. Reproduced with permission from ref 44. Copyright 2022 Wiley-VCH. (g) Coaxial printing was used to prepare conductive composite structures. Reproduced with permission from ref 58. Copyright 2023 Springer Nature. (h) A tactile sensor composed of flexible magnetic film and Hall sensor. Reproduced with permission from ref 59. Copyright 2022 American Chemical Society. (i) Wearable power generation device was achieved via the giant magnetoelastic effect. Reproduced with permission from ref 60. Copyright 2021 Springer Nature.

4.3. Biomedical Applications of Miniature Magnetic Soft Machines

Magnetically actuated soft robots offer a promising option for in vivo delivery of therapeutic agents due to their deep penetration and controllability.[61] Attributed to the development of preparation strategies, delivery systems crossing different scales have been validated. For instance, a magnetic soft machine developed using a pH-responsive hydrogel can serve as a drug carrier for local therapy of cancer cells within an artificial blood vessel network.[6] To safely retrieve non-therapeutic components, magnetic soft machines with detachable capabilities will be highly preferred. For instance, soluble tape can be utilized to temporarily secure the therapeutic agent, allowing it to be delivered at the lesion site (Figure 7a).[9] Once the target location is reached, the tape

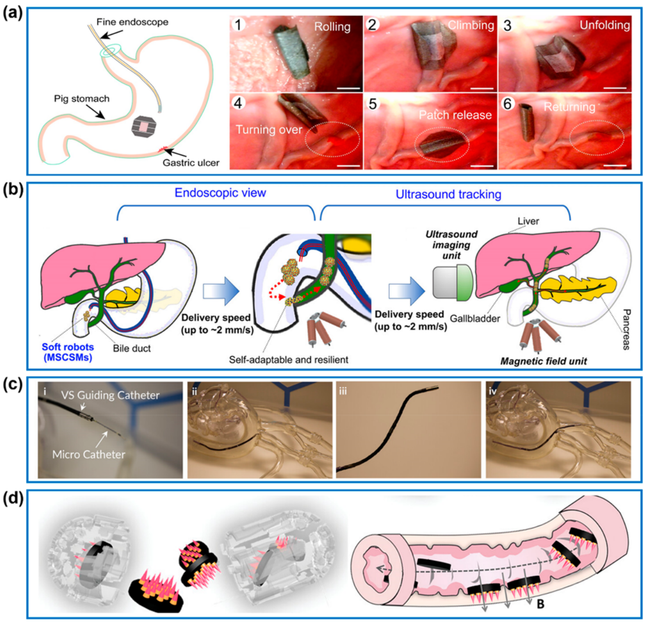


Figure 7. Biomedical applications of magnetic miniature soft machines. (a) Therapy patch transfer by soft robot in stomach. Reproduced with permission from ref 9. Copyright 2022 American Academy for the Advancement of Science. (b) Active and rapid delivery to deep and narrow space using soft microrobots. Reproduced with permission from ref 4. Copyright 2021 American Academy for the Advancement of Science. (c) Variable stiffness magnetic catheter. Reproduced with permission from ref 63. Copyright 2021 Wiley-VCH. (d) Microneedle robots are encapsulated in enteric capsules. Reproduced with permission from ref 65. Copyright 2021 Wiley-VCH.

can be dissolved, leaving the therapeutic agent and safely recycling the remaining robotic structure. In addition, in vivo targeted delivery is often limited by the accessible space and delivery duration. Our group proposed a soft machine that fuses cell spheroids and magnetic nanoparticles, combined with endoscopic technology, to achieve rapid and precise delivery within the bile duct (Figure 7b).[4]

In addition to delivery systems, magnetic soft machines find wide application in medical devices for performing diverse minimally invasive surgeries.[18,62] The magneto-elastomer based continuum robots have demonstrated capability of omnidirectional steering under programmable magnetic inputs, and navigation in tortuous environments combined with medical imaging.[63,64] To enhance the dexterity of the magnetic catheter and adapt it to different working environments, variable stiffness is an important feature. Shape memory polymers and low-melting alloys have been applied to variable stiffness catheters whose stiffness can be regulated by Joule heating (Figure 7c).[63] This variable stiffness magnetic catheter can maintain high stiffness when precise operations are required while exhibiting soft properties to navigate through tortuous space. Active capsule devices have demonstrated capabilities in the diagnosis and treatment of gastrointestinal diseases. Zhao et al. encapsulated magnetic microneedles within a commercially available capsule, enabling its delivery to the small intestine tissue through oral delivery system (Figure 7d).[65] Upon the disintegration of the capsule and application of an external magnetic field, the magnetic microneedles can penetrate the small intestine, facilitating the release of insulin.

5. CONCLUSIONS AND PERSPECTIVES

This Account provides an overview of different types of magnetic soft machines and presents our recent progress in programmable magnetization and reconfigurable morphological transformation. Although magnetic soft machines hold significant potential for various applications, their practical implementation, particularly in commercial settings, remains constrained due to several technical and scientific challenges. The manipulation strategies employed by magnetic soft machines currently face challenges in terms of low efficiency and limited collaborative capabilities. Despite extensive research on collaborative and independent control, the number of objects that can be effectively controlled remains limited. Therefore, conducting in-depth research on automated control of magnetic soft machines will be crucial in addressing these limitations and advancing their capabilities. The development of reconfigurable flexible electronic devices utilizing magnetic soft matter presents challenges related to the coupling of sensing targets, resolution, and interface connections during the arrangement of sensing units. To address these challenges, there is significant potential in the creation of magnetic soft machines that are fully flexible, possess stable interface connections, and offer distributed sensing capabilities. In this regard, the integration of multiple sensing units through multimaterial 3D printing technology is expected to facilitate seamless advancements in this field.

When it comes to in vivo medical applications, the development of magnetic control systems remains highly challenging, requiring careful consideration of factors such as the effective working space and the complexity and potential hazards associated with the movement of permanent magnets or electromagnetic coils. In addition, there is still much work to be done in order to facilitate their practical implementation, especially regarding the biocompatibility, biodegradability, and environmental adaptability of these soft machines. First, when targeting in vivo surgery, the biosafety of magnetic agents and the handling of the magnetic soft machines after treatment need to be carefully considered. It has been reported that magnetic particles Co and Ni are toxic, while FePt and Fe_3O_4 particles are biocompatible. The exploration of magnetic particles with nonimmunogenic, noncytotoxic, sufficient responsiveness, and ease-preparation is of great significance. Achieving biodegradability in miniature soft machines entails the complete degradation or retrieval of these machines within the human body after performing in vivo medical tasks with the degraded products being biosafe. This poses a significant challenge for both matrix materials and magnetic agents. Currently, gelatin methacryloyl has garnered considerable attention as a type of degradable polymer. It not only allows for photopolymerization but also can be digested through the action of protease. While the range of available degradable materials is expanding, the number of degradable magnetic agents remains limited, and there is room for improvement in processing biodegradable materials at the micrometer scale to meet specific shape and functional requirements. In addition, the adaptability of magnetic soft machines to their environment enables them to effectively navigate complex in vivo settings, ensuring optimal performance. The geometric shape and mechanical response characteristics of miniaturized soft machines play a crucial role as design indicators in the development of biomedical devices, including stents and catheters. To accommodate the intricate morphology of biological tissues, extensive research has been devoted to 3D curved surfaces, with a particular emphasis on the inverse design approach. As highlighted in section 3.4, challenges persist in the theoretical and methodological aspects of reverse designing curved surface morphology for magnetic soft machines. There is still extensive space for exploration in encoding 3D magnetic domains in magnetic soft materials. Furthermore, given the nonlinear mechanical responsiveness of biological soft tissue, it is imperative to explore the regulation of magnetic soft matter in order to align with its mechanical properties. This pursuit represents a crucial development direction for advancing future magnetic soft machines. Finally, autonomous navigation of magnetic soft machines in unknown environments is a key challenge for their in vivo medical applications. We need to rationally apply cutting-edge medical imaging technology and explore control algorithms with different levels of autonomy to enhance the environmental adaptability of magnetic soft machines.[66−69]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/accountsmr.3c00227.

Comparison of different stimuli-responsive soft machines and comparison of different types of magnetic soft machines (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Dongdong Jin − *School of Materials Science and Engineering, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, China*; Email: jindongdong@hit.edu.cn

Li Zhang − *Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, Hong Kong, China; Chow Yuk Ho Technology Center for Innovative Medicine, The Chinese University of Hong Kong, Hong Kong, China; CUHK T Stone Robotics Institute and Department of Surgery, The Chinese University of Hong Kong, Hong Kong, China*; orcid.org/0000-0003-1152-8962; Email: lizhang@mae.cuhk.edu.hk

Author

Neng Xia − *Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, Hong Kong, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/accountsmr.3c00227

Notes

The authors declare no competing financial interest.

Biographies

Neng Xia received his Ph.D. in Mechanical and Automation Engineering from The Chinese University of Hong Kong in 2023 and currently is a postdoctoral fellow in the Department of Mechanical and Automation Engineering. His research interests focus on the magnetic soft robots and 3D printing.

Dongdong Jin is currently an Associate Professor in the School of Materials Science and Engineering at Harbin Institute of Technology (Shenzhen). He received his Bachelor and Master degrees from Zhejiang University, and Ph.D. from The Chinese University of Hong Kong (CUHK) in 2020. He then worked as a postdoctoral fellow in CUHK and joined Harbin Institute of Technology (Shenzhen) in 2022. His research interests focus on the construction and functionalization of reconfigurable soft-matter robotics at small scale.

Li Zhang is a Professor in the Department of Mechanical and Automation Engineering and a Professor by Courtesy in the Department of Surgery at The Chinese University of Hong Kong. He is also a director of the Shenzhen Institutes of Advanced Technology of the Chinese Academy of Sciences—CUHK Joint Laboratory of Robotics and Intelligent Systems. His main research interests include small-scale robotics and their applications for translational biomedicine.

■ ACKNOWLEDGMENTS

The work is financially supported by the Hong Kong Research Grants Council (RGC) with project Nos. RFS2122-4S03, GRF 14301122, GRF 14300621, E-CUHK401/20; the ITF project with Project No MRP/036/18X funded by the HKSAR Innovation and Technology Commission (ITC); the Croucher Foundation Grant with ref. no. CAS20403; the Research Impact Fund (project no. R4015-21); Research Fellow Scheme (project no. RFS2122-4S03) from the Research Grants Council (RGC) of Hong Kong, and the CUHK internal grants. The authors also thank the support from Multi-Scale Medical Robotics Centre (MRC), InnoHK, at the Hong Kong Science Park, and the SIAT-CUHK Joint Laboratory of Robotics and Intelligent Systems.

■ REFERENCES

(1) Cianchetti, M.; Laschi, C.; Menciassi, A.; Dario, P. Biomedical applications of soft robotics. *Nat. Rev. Mater.* **2018**, *3*, 143−153.

(2) Yang, L.; Yu, J.; Yang, S.; Wang, B.; Nelson, B. J.; Zhang, L. A survey on swarm microrobotics. *IEEE Trans. Robot.* **2022**, *38*, 1531−1551.

(3) Zhang, C.; Pan, C.; Chan, K.; Gao, J.; Yang, Z.; Leung, K.; Jin, D.; Wang, Y.; Xia, N.; Ning, Z.; et al. Wirelessly powered deformable electronic stent for noninvasive electrical stimulation of lower esophageal sphincter. *Sci. Adv.* **2023**, *9*, No. eade8622.

(4) Wang, B.; Chan, K. F.; Yuan, K.; Wang, Q.; Xia, X.; Yang, L.; Ko, H.; Wang, Y.-X. J.; Sung, J. J. Y.; Chiu, P. W. Y.; et al. Endoscopy-assisted magnetic navigation of biohybrid soft microrobots with rapid endoluminal delivery and imaging. *Sci. Robot.* **2021**, *6*, No. eabd2813.

(5) Jin, D.; Yuan, K.; Du, X.; Wang, Q.; Wang, S.; Zhang, L. Domino reaction encoded heterogeneous colloidal microswarm with on-demand morphological adaptability. *Adv. Mater.* **2021**, *33*, No. 2100070.

(6) Xin, C.; Jin, D.; Hu, Y.; Yang, L.; Li, R.; Wang, L.; Ren, Z.; Wang, D.; Ji, S.; Hu, K.; et al. Environmentally adaptive shape-morphing microrobots for localized cancer cell treatment. *ACS Nano* **2021**, *15*, 18048−18059.

(7) Kim, J.; Chung, S. E.; Choi, S.-E.; Lee, H.; Kim, J.; Kwon, S. Programming magnetic anisotropy in polymeric microactuators. *Nat. Mater.* **2011**, *10*, 747−752.

(8) Zhang, J.; Ren, Z.; Hu, W.; Soon, R. H.; Yasa, I. C.; Liu, Z.; Sitti, M. Voxelated three-dimensional miniature magnetic soft machines via multimaterial heterogeneous assembly. *Sci. Robot.* **2021**, *6*, No. eabf0112.

https://doi.org/10.1021/accountsmr.3c00227
Acc. Mater. Res. 2024, 5, 173−183

(9) Dong, Y.; Wang, L.; Xia, N.; Yang, Z.; Zhang, C.; Pan, C.; Jin, D.; Zhang, J.; Majidi, C.; Zhang, L. Untethered small-scale magnetic soft robot with programmable magnetization and integrated multifunctional modules. *Sci. Adv.* **2022**, *8*, No. eabn8932.
(10) Jin, D.; Wang, Q.; Chan, K. F.; Xia, N.; Yang, H.; Wang, Q.; Yu, S. C. H.; Zhang, L. Swarming self-adhesive microgels enabled aneurysm on-demand embolization in physiological blood flow. *Sci. Adv.* **2023**, *9*, No. eadf9278.
(11) Wang, Q.; Zhang, L. External power-driven microrobotic swarm: from fundamental understanding to imaging-guided delivery. *ACS Nano* **2021**, *15*, 149−174.
(12) Ji, F.; Wu, Y.; Pumera, M.; Zhang, L. Collective behaviors of active matter learning from natural taxes across scales. *Adv. Mater.* **2023**, *35*, No. 2203959.
(13) Cai, L.; Wang, H.; Yu, Y.; Bian, F.; Wang, Y.; Shi, K.; Ye, F.; Zhao, Y. Stomatocyte structural color-barcode micromotors for multiplex assays. *Natl. Sci. Rev.* **2020**, *7*, 644−651.
(14) Chen, H.; Miao, S.; Zhao, Y.; Luo, Z.; Shang, L. Rotary Structural Color Spindles from Droplet Confined Magnetic Self-Assembly. *Adv. Sci.* **2023**, *10*, No. 2207270.
(15) Tariq, A.; Arif, Z. U.; Khalid, M. Y.; Hossain, M.; Rasool, P. I.; Umer, R.; Ramakrishna, S. Recent advances in the additive manufacturing of stimuli-responsive soft polymers. *Adv. Eng. Mater.* **2023**, *25*, No. 2301074.
(16) Lucarini, S.; Hossain, M.; Garcia-Gonzalez, D. Recent advances in hard-magnetic soft composites: Synthesis, characterisation, computational modelling, and applications. *Compos. Struct.* **2022**, *279*, No. 114800.
(17) Kim, Y.; Zhao, X. Magnetic soft materials and robots. *Chem. Rev.* **2022**, *122*, 5317−5364.
(18) Yang, Z.; Yang, H.; Cao, Y.; Cui, Y.; Zhang, L. Magnetically Actuated Continuum Medical Robots: A Review. *Adv. Intell. Syst.* **2023**, *5*, No. 2200416.
(19) Yang, L.; Zhang, L. Motion control in magnetic microrobotics: From individual and multiple robots to swarms. *Annu. Rev. Control Robot. Auton. Syst.* **2021**, *4*, 509−534.
(20) Yang, Z.; Zhang, L. Magnetic actuation systems for miniature robots: A review. *Adv. Intell. Syst.* **2020**, *2*, No. 2000082.
(21) Sun, M.; Hao, B.; Yang, S.; Wang, X.; Majidi, C.; Zhang, L. Exploiting ferrofluidic wetting for miniature soft machines. *Nat. Commun.* **2022**, *13*, No. 7919.
(22) Sun, M.; Tian, C.; Mao, L.; Meng, X.; Shen, X.; Hao, B.; Wang, X.; Xie, H.; Zhang, L. Reconfigurable magnetic slime robot: deformation, adaptability, and multifunction. *Adv. Funct. Mater.* **2022**, *32*, No. 2112508.
(23) Wang, B.; Kostarelos, K.; Nelson, B. J.; Zhang, L. Trends in micro-/nanorobotics: materials development, actuation, localization, and system integration for biomedical applications. *Adv. Mater.* **2021**, *33*, No. 2002047.
(24) Yarali, E.; Baniasadi, M.; Zolfagharian, A.; Chavoshi, M.; Arefi, F.; Hossain, M.; Bastola, A.; Ansari, M.; Foyouzat, A.; Dabbagh, A.; et al. Magneto-/electro-responsive polymers toward manufacturing, characterization, and biomedical/soft robotic applications. *Appl. Mater. Today* **2022**, *26*, No. 101306.
(25) Dong, Y.; Wang, L.; Iacovacci, V.; Wang, X.; Zhang, L.; Nelson, B. J. Magnetic helical micro-/nanomachines: Recent progress and perspective. *Matter* **2022**, *5*, 77−109.
(26) Ma, Z.; Mohapatra, J.; Wei, K.; Liu, J. P.; Sun, S. Magnetic nanoparticles: Synthesis, anisotropy, and applications. *Chem. Rev.* **2023**, *123*, 3904−3943.
(27) Bastola, A. K.; Hossain, M. The shape-morphing performance of magnetoactive soft materials. *Mater. Des.* **2021**, *211*, No. 110172.
(28) Bastola, A. K.; Hossain, M. A review on magneto-mechanical characterizations of magnetorheological elastomers. *Compos. B. Eng.* **2020**, *200*, No. 108348.
(29) Mirvakili, S. M.; Hunter, I. W. Artificial muscles: Mechanisms, applications, and challenges. *Adv. Mater.* **2018**, *30*, No. 1704407.
(30) Deng, Z.; Dapino, M. J. Review of magnetostrictive materials for structural vibration control. *Smart. Mater. Struct.* **2018**, *27*, No. 113001.
(31) Cui, J.; Huang, T.-Y.; Luo, Z.; Testa, P.; Gu, H.; Chen, X.-Z.; Nelson, B. J.; Heyderman, L. J. Nanomagnetic encoding of shape-morphing micromachines. *Nature* **2019**, *575*, 164−168.
(32) Magdanz, V.; Khalil, I. S.; Simmchen, J.; Furtado, G. P.; Mohanty, S.; Gebauer, J.; Xu, H.; Klingner, A.; Aziz, A.; Medina-Sánchez, M.; et al. IRONSperm: Sperm-templated soft magnetic microrobots. *Sci. Adv.* **2020**, *6*, No. eaba5855.
(33) Alapan, Y.; Yigit, B.; Beker, O.; Demirörs, A. F.; Sitti, M. Shape-encoded dynamic assembly of mobile micromachines. *Nat. Mater.* **2019**, *18*, 1244−1251.
(34) Deng, H.; Sattari, K.; Xie, Y.; Liao, P.; Yan, Z.; Lin, J. Laser reprogramming magnetic anisotropy in soft composites for reconfigurable 3D shaping. *Nat. Commun.* **2020**, *11*, No. 6325.
(35) Song, H.; Lee, H.; Lee, J.; Choe, J. K.; Lee, S.; Yi, J. Y.; Park, S.; Yoo, J.-W.; Kwon, M. S.; Kim, J. Reprogrammable ferromagnetic domains for reconfigurable soft magnetic actuators. *Nano Lett.* **2020**, *20*, 5185−5192.
(36) Shen, Y.; Jin, D.; Fu, M.; Liu, S.; Xu, Z.; Cao, Q.; Wang, B.; Li, G.; Chen, W.; Liu, S.; et al. Reactive wetting enabled anchoring of non-wettable iron oxide in liquid metal for miniature soft robot. *Nat. Commun.* **2023**, *14*, No. 6276.
(37) Hu, W.; Lum, G. Z.; Mastrangeli, M.; Sitti, M. Small-scale soft-bodied robot with multimodal locomotion. *Nature* **2018**, *554*, 81−85.
(38) Zheng, Z.; Wang, H.; Demir, S. O.; Huang, Q.; Fukuda, T.; Sitti, M. Programmable aniso-electrodeposited modular hydrogel microrobots. *Sci. Adv.* **2022**, *8*, No. eade6135.
(39) Xia, N.; Jin, D.; Pan, C.; Zhang, J.; Yang, Z.; Su, L.; Zhao, J.; Wang, L.; Zhang, L. Dynamic morphological transformations in soft architected materials via buckling instability encoded heterogeneous magnetization. *Nat. Commun.* **2022**, *13*, No. 7514.
(40) Chen, H.; Zhang, H.; Dai, Y.; Zhu, H.; Hong, G.; Zhu, C.; Qian, X.; Chai, R.; Gao, X.; Zhao, Y. Magnetic Hydrogel Microrobots Delivery System for Deafness Prevention. *Adv. Funct. Mater.* **2023**, *33*, No. 2303011.
(41) Arif, Z. U.; Khalid, M. Y.; Tariq, A.; Hossain, M.; Umer, R. 3D printing of stimuli-responsive hydrogel materials: Literature review and emerging applications. *Giant* **2024**, *17*, No. 100209.
(42) Zhu, G.; Hou, Y.; Xia, N.; Wang, X.; Zhang, C.; Zheng, J.; Jin, D.; Zhang, L. Fully Recyclable, Healable, Soft, and Stretchable Dynamic Polymers for Magnetic Soft Robots. *Adv. Funct. Mater.* **2023**, *33*, No. 2300888.
(43) Sun, M.; Yang, S.; Jiang, J.; Zhang, L. Horizontal and vertical coalescent microrobotic collectives using ferrofluid droplets. *Adv. Mater.* **2023**, *35*, No. 2300521.
(44) Wang, B.; Zhang, B.; Tan, Y.; Ji, F.; Lv, G.; Pan, C.; Handschuh-Wang, S.; Zhang, L.; Zhou, X. Leech-Inspired Shape-Encodable Liquid Metal Robots for Reconfigurable Circuit Welding and Transient Electronics. *Adv. Intell. Syst.* **2022**, *4*, No. 2200080.
(45) Hu, X.; Yasa, I. C.; Ren, Z.; Goudu, S. R.; Ceylan, H.; Hu, W.; Sitti, M. Magnetic soft micromachines made of linked microactuator networks. *Sci. Adv.* **2021**, *7*, No. eabe8436.
(46) Xu, T.; Zhang, J.; Salehizadeh, M.; Onaizah, O.; Diller, E. Millimeter-scale flexible robots with programmable three-dimensional magnetization and motions. *Sci. Robot.* **2019**, *4*, No. eaav4494.
(47) Xia, N.; Jin, B.; Jin, D.; Yang, Z.; Pan, C.; Wang, Q.; Ji, F.; Iacovacci, V.; Majidi, C.; Ding, Y.; et al. Decoupling and reprogramming the wiggling motion of midge larvae using a soft robotic platform. *Adv. Mater.* **2022**, *34*, No. 2109126.
(48) Kim, Y.; Yuk, H.; Zhao, R.; Chester, S. A.; Zhao, X. Printing ferromagnetic domains for untethered fast-transforming soft materials. *Nature* **2018**, *558*, 274−279.
(49) Khalid, M. Y.; Arif, Z. U.; Ahmed, W.; Umer, R.; Zolfagharian, A.; Bodaghi, M. 4D printing: Technological developments in robotics applications. *Sens. Actuator. A. Phys.* **2022**, *343*, 113670.
(50) Wu, S.; Ze, Q.; Zhang, R.; Hu, N.; Cheng, Y.; Yang, F.; Zhao, R. Symmetry-breaking actuation mechanism for soft robotics and

active metamaterials. *ACS Appl. Mater. Interfaces* **2019**, *11*, 41649−41658.

(51) Novelino, L. S.; Ze, Q.; Wu, S.; Paulino, G. H.; Zhao, R. Untethered control of functional origami microrobots with distributed actuation. *Proc. Natl. Acad. Sci. U. S. A.* **2020**, *117*, 24096−24101.

(52) Ze, Q.; Wu, S.; Dai, J.; Leanza, S.; Ikeda, G.; Yang, P. C.; Iaccarino, G.; Zhao, R. R. Spinning-enabled wireless amphibious origami millirobot. *Nat. Commun.* **2022**, *13*, No. 3118.

(53) Kuang, X.; Wu, S.; Ze, Q.; Yue, L.; Jin, Y.; Montgomery, S. M.; Yang, F.; Qi, H. J.; Zhao, R. Magnetic dynamic polymers for modular assembling and reconfigurable morphing architectures. *Adv. Mater.* **2021**, *33*, No. 2102113.

(54) Zhu, H.; Wang, Y.; Ge, Y.; Zhao, Y.; Jiang, C. Kirigami-Inspired Programmable Soft Magnetoresponsive Actuators with Versatile Morphing Modes. *Adv. Sci.* **2022**, *9*, No. 2203711.

(55) Jiang, S.; Li, B.; Zhao, J.; Wu, D.; Zhang, Y.; Zhao, Z.; Zhang, Y.; Yu, H.; Shao, K.; Zhang, C.; et al. Magnetic Janus origami robot for cross-scale droplet omni-manipulation. *Nat. Commun.* **2023**, *14*, No. 5455.

(56) Dong, X.; Sitti, M. Controlling two-dimensional collective formation and cooperative behavior of magnetic microrobot swarms. *Int. J. Rob. Res.* **2020**, *39*, 617−638.

(57) Ze, Q.; Kuang, X.; Wu, S.; Wong, J.; Montgomery, S. M.; Zhang, R.; Kovitz, J. M.; Yang, F.; Qi, H. J.; Zhao, R. Magnetic shape memory polymers with integrated multifunctional shape manipulation. *Adv. Mater.* **2020**, *32*, No. 1906657.

(58) Zhang, Y.; Pan, C.; Liu, P.; Peng, L.; Liu, Z.; Li, Y.; Wang, Q.; Wu, T.; Li, Z.; Majidi, C.; et al. Coaxially printed magnetic mechanical electrical hybrid structures with actuation and sensing functionalities. *Nat. Commun.* **2023**, *14*, No. 4428.

(59) Hu, H.; Zhang, C.; Pan, C.; Dai, H.; Sun, H.; Pan, Y.; Lai, X.; Lyu, C.; Tang, D.; Fu, J.; et al. Wireless flexible magnetic tactile sensor with super-resolution in large-areas. *ACS Nano* **2022**, *16*, 19271−19280.

(60) Zhou, Y.; Zhao, X.; Xu, J.; Fang, Y.; Chen, G.; Song, Y.; Li, S.; Chen, J. Giant magnetoelastic effect in soft systems for bioelectronics. *Nat. Mater.* **2021**, *20*, 1670−1676.

(61) Sun, M.; Chan, K. F.; Zhang, Z.; Wang, L.; Wang, Q.; Yang, S.; Chan, S. M.; Chiu, P. W. Y.; Sung, J. J. Y.; Zhang, L. Magnetic microswarm and fluoroscopy-guided platform for biofilm eradication in biliary stents. *Adv. Mater.* **2022**, *34*, No. 2201888.

(62) Cao, Y.; Yang, Z.; Hao, B.; Wang, X.; Cai, M.; Qi, Z.; Sun, B.; Wang, Q.; Zhang, L. Magnetic Continuum Robot with Intraoperative Magnetic Moment Programming. *Soft Robot.* **2023**, *10*, 1209−1223.

(63) Mattmann, M.; De Marco, C.; Briatico, F.; Tagliabue, S.; Colusso, A.; Chen, X. Z.; Lussi, J.; Chautems, C.; Pané, S.; Nelson, B. Thermoset shape memory polymer variable stiffness 4D robotic catheters. *Adv. Sci.* **2022**, *9*, No. 2103277.

(64) Yang, Z.; Yang, L.; Zhang, M.; Xia, N.; Zhang, L. Ultrasound-guided wired magnetic microrobot with active steering and ejectable tip. *IEEE Trans. Ind. Electron.* **2023**, *70*, 614−623.

(65) Zhang, X.; Chen, G.; Fu, X.; Wang, Y.; Zhao, Y. Magneto-Responsive Microneedle Robots for Intestinal Macromolecule Delivery. *Adv. Mater.* **2021**, *33*, No. 2104932.

(66) Yang, L.; Jiang, J.; Gao, X.; Wang, Q.; Dou, Q.; Zhang, L. Autonomous environment-adaptive microrobot swarm navigation enabled by deep learning-based real-time distribution planning. *Nat. Mach. Intell.* **2022**, *4*, 480−493.

(67) Cai, M.; Wang, Q.; Qi, Z.; Jin, D.; Wu, X.; Xu, T.; Zhang, L. Deep Reinforcement Learning Framework-Based Flow Rate Rejection Control of Soft Magnetic Miniature Robots. *IEEE Trans. Cybern.* **2023**, *53*, 7699−7711.

(68) Wang, Q.; Chan, K. F.; Schweizer, K.; Du, X.; Jin, D.; Yu, S. C. H.; Nelson, B. J.; Zhang, L. Ultrasound Doppler-guided real-time navigation of a magnetic microswarm for active endovascular delivery. *Sci. Adv.* **2021**, *7*, No. eabe5914.

(69) Wang, Q.; Du, X.; Jin, D.; Zhang, L. Real-time ultrasound doppler tracking and autonomous navigation of a miniature helical robot for accelerating thrombolysis in dynamic blood flow. *ACS Nano* **2022**, *16*, 604−616.

https://doi.org/10.1021/accountsmr.3c00227
Acc. Mater. Res. 2024, 5, 173−183