Enhanced Locomotion of Shape Morphing Microrobots by Surface Coating

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Mobile microrobots with shape morphing capability show great advantages for conducting tasks in complex environments. Combination of magnetically driven locomotion and stimuli-responsive shape morphing is an effective strategy to realize these microrobots. However, most existing microrobots fabricated by the combination strategy are of low locomotion efficiency due to the limited amount of magnetic material loaded. Herein, a novel scheme for coating the magnetic nanoparticles (NPs) on the surface of microrobot is proposed to increase the magnetic material loading amount. Theoretical analyses demonstrate that, below a critical size at microscale, surface coating NPs can load more magnetic material than embedding NPs into the volume due to the high surface area-to-volume ratio. Microrobots with both shape morphing and enhanced magnetically driven locomotion are fabricated by coating magnetic NPs on the surface of stimuli-responsive hydrogel microstructures. It is experimentally demonstrated that surface coating ensures that the microstructure has not only an efficient locomotion but also an excellent deformability. A four-claw microgripper is fabricated, which is smaller and has higher magnetically driven locomotion speed than the most existing shape morphing microrobots. This microgripper demonstrating carrying and delivery capabilities is of immediate interest to microobject manipulation and minimally invasive surgery.

1. Introduction

Microrobots have shown great potential in minimally invasive surgery, targeted therapy, and biological manipulation.[1,2] The features of excellent shape morphing and highly efficient locomotion are very important for microrobots. To take the microgripper and microstent as examples, shape morphing is essential for grasping or unfolding,[3] and efficient locomotion is necessary for the transport of the microrobots to a defined position.[4] Magnetically driven microrobots can achieve rapid locomotion with a controllable change in direction and have advantages of noncontact, harmless to living organisms,[5,6] To develop magnetic microrobots with shape morphing ability, methods such as introducing flexible joints/hinges[7,8] or combining magnetic nanoparticles (NPs) with stimuli-responsive materials[9,10] were developed. Joints/hinges significantly increase the shape morphing ability of the microrobot, while the fabricating process of the microrobot with joints/hinges is complicated.[8] In contrast, combining magnetic NPs with stimuli-responsive materials ensures that the microrobot not only performs an excellent deformability but also avoids the complicated fabricating process.

Stimuli-responsive hydrogels which are able to swell and shrink in response to different stimuli such as temperature, pH, and light represent a promising strategy to fabricate shape morphing microstructures.[9,10] Inhomogeneous swelling/shrinking of hydrogel microstructures results in bending, twisting, folding, and even more complex deformation.[11,12] The deformable microstructures can be fabricated by advanced manufacturing such as two-photon direct laser writing (DLW) system,[13,14] UV lithography,[15] and projection microstereolithography.[16] Thus, combining stimuli-responsive hydrogels with magnetic materials provides an attractive solution to fabricate microrobots with both shape morphing and locomotion abilities.[17]

To magnetically drive a hydrogel microstructure, magnetic material must be incorporated into the polymeric portions. In general, two typical methods can be used to add magnetic material. One is mixing the magnetic particles into the uncured material to obtain structures with particles embedded in volume,[18–21] i.e., volume embedding structures. The other is depositing the magnetic particles on the surface of the polymer portions[22–24] or oil-in-water self-assembly[25] to obtain structures with particles coated on the surface, i.e., surface coating structures. Thus, certain microrobots could locomote under the actuation of external magnetic field and deform flexibly in response...
to the variance of pH or temperature. However, it is still a challenge to achieve a highly efficient locomotion for these microrobots because of the limited magnetic material loading. In this work, a novel scheme for coating the magnetic NPs on the surface of the microrobot is proposed to increase the magnetic material loading amount. Theoretical analyses demonstrate that the microrobots with magnetic surface coating structures potentially load more magnetic material than volume embedding structures at microscale. Microrobots with both shape morphing and enhanced magnetically driven locomotion are fabricated by coating magnetic NPs on the surface of stimuli-responsive hydrogel microstructures fabricated by using two-photon DLW. Shape morphing and locomotion analyses demonstrate that coating the magnetic NPs on the surface ensures that the microstructure has not only an efficient locomotion but also an excellent deformability. Finally, to illustrate the potential applications of microrobots with both shape morphing and locomotion abilities as cargo delivery vehicles, a four-claw micromanipulator is fabricated to achieve a high magnetically driven locomotion speed (2.8 body length s⁻¹) with pH-responsive shape morphing for grasping. The feasibility of the micromanipulator for object delivery is tested to show the capabilities of picking up, carrying to the target position, and releasing object with high locomotion performance.

2. Results

2.1. Magnetic Surface Coating Structure to Enhance Magnetic Actuation

In an external applied magnetic field, the magnetic torque \( \tau_m \) exerted on the microrobot is\(^{(28)} \)

\[
\tau_m = V_m \mathbf{M} \times \mathbf{B} \tag{1}
\]

where \( \mathbf{M} \) is the volume magnetization of the magnetic material in a magnetic field with magnetic flux density \( \mathbf{B} \) and \( V_m \) is the volume of magnetic material that is loaded in the microrobot. The magnetic force \( \mathbf{F}_m \) exerted on the microrobot is\(^{(28)} \)

\[
\mathbf{F}_m = V_m (\mathbf{M} \cdot \nabla) \mathbf{B} \tag{2}
\]

Equation (1) and (2) suggest that larger \( V_m \) will exert higher magnetic force and torque on the microrobot body, leading to a high-speed locomotion. To study how to load more magnetic material at microscale, the variation of the volume ratio \( V_o/V_i \) as a function of the scale of the microrobot is analyzed, where \( V_o \) and \( V_i \) are the volumes of magnetic material that is loaded in the microrobots by surface coating particles and volume embedding particles, respectively. \( V_o/V_i > 1 \) means that the loaded amount of magnetic material for surface coating structure is larger than that for volume embedding structure. Figure 1A shows the schematic diagram of magnetic microrobots with surface coating structure and volume embedding structure and the typical progress of fabricating these magnetic microrobots using two-photon DLW system.

Without loss of generality, we consider a magnetic microrobot with a volume \( V \). For volume embedding structure, the volume \( V_i \) of magnetic material that is loaded in microrobot is \( V_i = C_i \cdot V \), where \( C_i \) is the volume fraction (vol%) of magnetic particles that are embedded in the microrobot. In the case of surface coating structure, the volume \( V_o \) of magnetic material that is loaded in microrobot is \( V_o = t \cdot S \), with \( t \) being the thickness of surface coating and \( S \) the equivalent surface area of the microrobot. Thus, the volume ratio \( V_o/V_i \) could be given by

\[
\frac{V_o}{V_i} = \frac{t \cdot S}{C_i \cdot V} \approx \frac{t}{C_i} \frac{1}{L} \tag{3}
\]

where \( L \) is the feature length of microrobot and \( L^{-1} \) is proportional to the surface area-to-volume ratio \( S/V \). It can be seen from Equation (3) that \( V_o/V_i \) increases as the feature length \( L \) decreases, which indicates that the surface coating structure is preferable at small scales. We first use a ball-shaped microrobot with a radius \( r \) to analyze the preferable size ranges for the surface coating structure and the volume embedding structure, respectively. Then we generalize this analysis to the microrobots with arbitrary shapes.

The surface area-to-volume ratio \( S/V \) of the ball-shaped microrobot is \( (S/V)_{ball} = 3/r \), supposing \( t \ll r \), and thus Equation (3) is rewritten as

\[
\left( \frac{V_o}{V_i} \right)_{ball} = \frac{3t}{C_i} \frac{1}{r} \tag{4}
\]

In two-photon DLW printing, on the one hand there is an upper limit of \( C_i \) because the magnetic particles tend to aggregate with increase in \( C_i \), which will result in local heating, bubble generation, and structural damage during printing.\(^{(19,20)} \) Our experiments also confirm that the microstructures printed using hydrogel precursor embedded with a high concentration of NPs show many drawbacks (see details in Section S1 and Figure S1, Supporting Information). On the other hand, to the best of our knowledge, the thickness of magnetic NPs surface coating has not been reported. Thus, we use the coating thickness of depositing nickel on the surface of microrobots as a reference. According to the literature (Table S1, Supporting Information), both \( C_i \) and \( t \) are adjustable, with \( C_i \) ranging from 0 to 2 vol% and \( t \) from 90 to 300 nm. Supposing \( C_i = 2 \) vol% for volume embedding structure and \( t = 300 \) nm for surface coating structure, the volume ratio \( V_o/V_i \) given by Equation (4) is shown in Figure 1B. When the size of the ball-shaped microrobot is less than \( r_c \approx 45 \) µm, \( V_o/V_i > 1 \), which means that the surface coating structure potentially loads more magnetic material in the microrobots.

Among the microrobots with arbitrary shapes but the same volume, ball-shaped microrobot has the smallest surface area-to-volume ratio, and

\[
\frac{V_o}{V_i} = \frac{t}{C_i} \frac{S}{V} \geq \frac{t}{C_i} \left( \frac{S}{V} \right)_{ball} = \left( \frac{V_o}{V_i} \right)_{ball} \tag{5}
\]

Thus, it can be concluded that the surface coating structure could potentially load more magnetic material when the microrobots scale down to \( L < 45 \) µm for using two-photon DLW to print microstructures.
2.2. Fabrication of Microrobots with Magnetic Surface Coating Structure

Microrobots with magnetic surface coating structure capable of both shape morphing and magnetically driven locomotion were fabricated by coating magnetic NPs on the surface of stimuli-responsive hydrogel microstructures which were printed by using two-photon DLW. As a primary demonstration, a bilayer ribbon is designed as shown in Figure 2A, constructed with an LH layer (top layer) and an H layer (bottom layer). The LH layer consists of alternating slender strips of hydrogel with low degree of cross-linking (LD, green color) and hydrogel with high degree of cross-linking (HD, red color). The H layer is pure HD. The LH layer shows a larger volumetric change in response to pH stimuli than H layer because hydrogel with low degree of cross-linking is more sensitive to changes in environments.\[13\]

The LD and HD strip patterns present an angle $\theta$ with respect to the bilayer ribbon. Figure 2B–D shows the fabrication process of a bilayer ribbon-shaped microrobot presented in Figure 2A. First, the microstructures were printed on a glass substrate using pH-response hydrogel precursor via two-photon DLW. The cross-linking degree of these microstructures can be tuned by the laser power and the scan speed of two-photon DLW. After printing, the microstructures were developed in isopropanol for 30 min. Second, the microstructures were put in a cubic container with the size $10 \text{ mm} \times 10 \text{ mm} \times 6 \text{ mm}$, and a certain volume of $\text{Fe}_3\text{O}_4/\text{ethyl lactate (Fe}_3\text{O}_4/\text{EL)}$ suspension was added to the container. After the complete evaporation of EL, $\text{Fe}_3\text{O}_4$ NPs were coated on the surface of the microstructures. Third, after a spinning coating of PAAm hydrogel precursor and an exposure to UV (365 nm) light for 5 s, a thin film of PAAm hydrogel with low degree of cross-linking was formed on the surface of the microstructure to prevent the shedding of $\text{Fe}_3\text{O}_4$ NPs from coating surface. Finally, the bilayer ribbons irreversibly deform to coiled ribbons to form microrobots when they were immersed into water. Figure 2E shows the designed structures for printing, the 3D structures after immersing into water, and the experimental images of three kinds of microrobots based on the bilayer ribbon.

The concentration and the volume of $\text{Fe}_3\text{O}_4/\text{EL}$ suspension were regulated to determine the $\text{Fe}_3\text{O}_4$ NPs coating thickness. Increasing the concentration as well as the volume of $\text{Fe}_3\text{O}_4/\text{EL}$ suspension added in the cubic container result in an increase in the coating thickness. The coating thicknesses were measured by scanning electron microscopy (SEM), as shown in Figure S2, Supporting Information. The thickness of the coating on microstructure is difficult to characterize, the thickness of the coating on the glass substrate was measured instead. Thicknesses of 0.7, 2.1, 3.3, and 5.1 $\mu$m $\text{Fe}_3\text{O}_4$ NPs coating were obtained by adding 200 $\mu$L of 5 mg mL$^{-1}$ $\text{Fe}_3\text{O}_4/\text{EL}$ suspension.

**Figure 1.** Schematic diagram of magnetic microrobots with surface coating structure and volume embedding structure. A) The typical fabrication progress of magnetic microrobots with surface coating structure and volume embedding structure. B) The comparison of magnetic material volume loaded in surface coating structure and volume embedding structure. The dashed line is $V_o/V_i = 1$. The dashdot line represents the critical size $r_c$.  

**Figure 2.** A) Fabrication process of microrobots with magnetic surface coating structure. B) Fabrication process of microrobots with volume embedding structure.
200 μL of 15 mg mL⁻¹ Fe₃O₄/EL suspension, 400 μL of 15 mg mL⁻¹ Fe₃O₄/EL suspension, and 600 μL of 15 mg mL⁻¹ Fe₃O₄/EL suspension in a 10 mm × 10 mm × 6 mm container, respectively. Ideally, the thickness of the surface coating can eventually be grown as much as desired until making the microrobot almost fully magnetic material. However, the coating thickness is limited by factors such as the deformability of the microrobots and the structural features of shape morphing. A thick coating might impair the deformability or conceal the structural features. Thus, to ensure a reasonable shape of the microstructure, the maximum thickness of the coating is designed to be comparable with the thickness of microstructure, i.e., 5 μm.

The validation of the coating approach was demonstrated with another two polymers: 1) polyethylene (glycol) diacrylate (PEGDA) hydrogel, which is a 3D printable hydrogel for two-photon DLW system; 2) polydimethylsiloxane, which is a silicone elastomer used in many applications (see details in Section S2 and Figure S3, Supporting Information). The SEM image of Fe₃O₄ NPs coated PEGDA hydrogel microstructure and polydimethylsiloxane microball is shown in Figure S3, Supporting Information. The manipulation of PEGDA hydrogel microstructure and polydimethylsiloxane microball under a magnetic field is shown in Figure S3, Supporting Information. Note that, apart from NPs coating, oil-in-water self-assembly is a powerful method for arranging magnetic NPs on the surface of polymer portions to obtain a high loading of magnetic NPs. However, the shape of microrobot formed by oil-in-water self-assembly is limited, mostly microspheres, while surface coating can be applied to fabricate a microstructure with complex shapes, which benefits the functional diversification.

2.3. Shape Morphing of Magnetic Microrobots

As the shape morphing ability of the microrobots originates from the deformation of hydrogel microstructures, the morphing
mode of microrobots and hydrogel microstructures without coating is analyzed with a coiled ribbon and a curved ribbon, as shown in Figure 3A, B. When the liquid environment changed from an acid solution (pH = 6) to an alkaline solution (pH = 11), the coiled ribbon unwound and transformed to the other coiled ribbon with a larger radius. The swelling differences between the HD and LD stripes resulted in the strain mismatch between LH layer and H-layer, leading to the unwinding deformation.[13] When the environment changed back to the acid solution, the coiled ribbon winded to its original shape. Figure 3B shows the bending and unbending modes of the curved ribbon with and without Fe3O4 NPs coating in the acid solution and alkaline solution.

To evaluate the influence of NPs coating on the deformability of the microrobot, curved ribbons (LH-layer thickness h1 = 4 μm, H-layer thickness h2 = 1 μm, width b = 20 μm, LD width l1 = 4 μm, HD width l2 = 4 μm, θ = 90°) with different coating thicknesses t (0, 2.1, 3.3, and 5.1 μm) were fabricated and the radii R′ of curved ribbons were measured, as shown in Figure 3C. It can be seen that in acid solution, the radii of the curved ribs with a coating thickness of 0, 2.1, 3.3, and 5.1 μm are 35.0, 40.9, 40.6, and 38.9 μm, respectively. In alkaline solution, they are 87.1, 82.2, 82.5, and 83.3 μm, respectively. The experimental data clearly show that the curve radius is almost independent of the coating thickness. The reason may lie in that when the microrobots were immersed in water, the hydrogel microstructures swell and the coating splits open, as shown in Figure 3D. The discontinuity of the NPs coating reduces the suppression effect of the coating on the deformation of the microrobot.

The shape morphing of the ribbon can be adjusted by regulating the thickness ratio h1/h2, the pattern parameter l1/l2, and the angle θ. A series of bilayer ribbons (Figure 3A) with different h1/h2 and l1/l2 were printed, and the corresponding non-dimensional radii R/(h1 + h2) were measured (see Figure S4, Supporting Information). The smaller h1/h2 or l1/l2, the larger R/(h1 + h2). As h1/h2 or l1/l2 increases, R/(h1 + h2) approaches a constant. The geometric dependence provides the guidance for designing the shape morphing of the ribbon.

2.4. Locomotion of Microrobots

In this section, the effect of loaded magnetic material amount on the locomotion performance of cuboid-shaped microrobots is investigated, as shown in Figure 4. A rotational magnetic field of 10 mT was used to drive the microrobots tumbling on a surface, as shown in Figure 4A and Movie S1, Supporting Information. Four samples with different amounts of Fe3O4 NPs coating (Table S2, Supporting Information) were fabricated, namely, S-1, S-2, S-3, and S-4 in sequence of increasing amount.
of NPs. The locomotion velocity \( \nu \) of the microrobot will change as a function of the applied rotational frequency \( f \) (Figure S5, Supporting Information). There exists a critical frequency for the locomotion of microrobots, i.e., the step-out frequency, at which maximum locomotion velocity is achieved. As shown in Figure 4B, the maximum locomotion velocities \( \nu_{\text{max}} \) of S-1, S-2, S-3, and S-4 are 232.1, 273.0, 280.3, and 280.6 \( \mu \text{m s}^{-1} \), respectively, which demonstrates that the more the loaded amount of Fe\(_3\)O\(_4\) NPs, the faster the locomotion of the microrobots. Meanwhile, the step-out frequencies of S-1, S-2, S-3, and S-4 are 4, 10, 12, and 16 Hz, respectively, which also increases as the amount of Fe\(_3\)O\(_4\) NPs increases. Theoretically, the step-out frequency \( f_{\text{step-out}} \) is expressed as (see Section S3, Supporting Information, for more details)

\[
 f_{\text{step-out}} = \frac{V_m}{2 \pi \kappa_d V_s \mu} |\mathbf{M}| |\mathbf{B}| \tag{6}
\]

where \( \kappa_d \) is a coefficient depending on the geometric shape of the microrobot, \( V_m \) is the volume of the microrobot, and \( \mu \) is the fluid viscosity. Equation (6) reveals that the step-out frequency of microrobots increases as the amount of surface coating Fe\(_3\)O\(_4\) NPs increases, which is consistent with the experimental results. The step-out frequency is not linearly proportional to the coated Fe\(_3\)O\(_4\) NPs amount, which might because that the shape transformation and adhesion to the substrate during tumbling motion are not considered in Equation (6).

### 2.5. Microgripper with High Locomotion Performance

Microobject delivery is one of the most important applications for microrobots, which requires the microrobots to have both shape morphing and locomotion abilities. A four-claw microgripper was designed and fabricated based on the bilayer ribbon with \( \theta = 90^\circ \), \( l_1 = l_2 = 4 \mu \text{m}, h_1 = 4 \mu \text{m}, \) and \( h_2 = 1 \mu \text{m} \). The volume and the concentration of the Fe\(_3\)O\(_4\)/EL suspension for surface coating were 200 \( \mu \text{L} \) and 15 mg mL\(^{-1} \), respectively. The designed in-plane microgripper with the size of 160 \( \mu \text{m} \times 160 \mu \text{m} \) (tip-to-tip) could transform into a curved microgripper with the size around 70–80 \( \mu \text{m} \), as long as the printed microgripper was immersed into water. Reversible opening and closing of the curved microgripper can be triggered by pH stimulation, as shown in Figure 5A.

First, we demonstrate the feasibility of the microgripper for object delivery. As shown in Figure 5B,C, the microgripper was immersed in an alkaline solution to stay open (State I, Place a) in the beginning. Then, the microgripper moved to the location above the object which is a polystyrene microball (State II, Place b) under the control of a magnetic field generated by a permanent magnet. By changing the alkaline solution into an acid solution, the microgripper was closed with the claws undergoing bending deformation. Thus, the object was grasped by the microgripper (State III, Place b). Under a magnetic field, the microgripper took the object to the final position (State III, Place c). Finally, by changing the acid solution back to an alkaline solution, the four claws of the microgripper experienced a time-related bending process\(^{[29]} \) (from State III, through State IV to State I), i.e., the claws further curved rapidly at first to release the object by squeezing it out (State IV, Place c) and subsequently deformed to the original shape in alkaline solution, as shown in Figure 5C and Movie S2, Supporting Information. The microgripper displays certain adaptability to the object as it can grasp ground irregular silica particle with a size around 50 \( \mu \text{m} \), as shown in Movie S3, Supporting Information.

Furthermore, the locomotion performance of the microgripper was examined. The velocity of microgripper varying as a function of the rotational frequency in the external magnetic field is shown in Figure 6A. The locomotion velocity of microgripper increases as the frequency increases when the rotation frequency ranges from 0 to 4 Hz, while the velocity decreases as the frequency further increases. Thus, the step-out frequency of the microgripper is 4 Hz and the maximum locomotion velocity of the microgripper is approximately 216 \( \mu \text{m s}^{-1} \). Then, the locomotion of microgripper carrying the object (a polystyrene microball) is also measured, in which the maximum locomotion velocity is approximately 271 \( \mu \text{m s}^{-1} \), as shown in Figure 6A. The locomotion velocity of microgripper carrying object is higher, while the step-out frequency is smaller than that of microgripper itself, which might result from the changed size and motion.

![Figure 4. Locomotion of cuboid-shaped microrobots coated with different amount of Fe\(_3\)O\(_4\) NPs. A) Diagram and video snapshots of a cuboid-shaped microrobot tumbling on surface under a rotational magnetic field of 10 mT, scale bar: 100 \( \mu \text{m} \). B) The maximum locomotion velocity \( \nu_{\text{max}} \) (inset: the step-out frequency \( f_{\text{step-out}} \)) of the cuboid-shaped microrobots coated with different amount of Fe\(_3\)O\(_4\) NPs.](image-url)
posture after grasping an object. The sizes of microgrippers with and without carrying object were measured via optical images (Figure S6, Supporting Information), which are 82 and 77 μm, respectively. The step-out frequency decreases as the volume $V_r$ of microrobot increases according to Equation (6), which is consistent with the experimental results.

Comparison of the locomotion performances among the existing soft microrobots with both shape morphing and magnetically driven locomotion abilities, several living organisms, and the microgripper in this work is shown in Figure 6B. Here, we quantify the speed as the locomotion distance in 1 s relative to the body length (BL). Thus, the speeds are...
2.8 and \( \approx 3.3 \text{ BL s}^{-1} \) for the microgripper itself and the microgripper carrying an object, respectively. As shown in Figure 6B, the speeds of the existing microrobots can reach up to 1.8 BL s\(^{-1}\), which clearly exhibit a lower locomotion efficiency than the microgripper in this work. Nevertheless, the speeds of living organisms are much higher. For example, *Escherichia coli* can move as fast as 11.2 BL s\(^{-1}\). In addition, the size of most of existing soft microrobots is about 1 mm, which is much larger than the living organisms and cannot be easily utilized in vivo, while it is the other advantage for the microgripper in this work that it is small enough to conduct complex task dexterously. The size of proposed microgripper is smaller than the most of existing microrobots, but the locomotion speed is higher. This work widens the size and the locomotion speed boundary for microrobots with both shape morphing and magnetically driven locomotion abilities.

### 2.6. The Biocompatibility of the Microrobots

To demonstrate the biocompatibility of the printed hydrogel microstructures and Fe\(_3\)O\(_4\) NPs, we cultured the L929 cell on the printed hydrogel microstructures with and without Fe\(_3\)O\(_4\) NPs coating, respectively, whose fluorescence images after culturing for 24 h are shown in Figure 7. It can be seen that the printed hydrogel microstructures with and without Fe\(_3\)O\(_4\) NPs coating presented adequate cell viability, which demonstrates the noncytotoxic property of the microrobots.

### 3. Conclusions

This work focuses on improving the magnetically driven locomotion performance of shape morphing microrobots by increasing the amount of magnetic material loaded in microrobots. Theoretical analyses demonstrate that, below a critical size at microscale, the microrobots with magnetic surface coating structure can load more magnetic material than that with magnetic volume embedding structure. Microrobots with excellent performances in shape morphing and magnetically driven locomotion are fabricated by coating magnetic NPs on the surface of pH-responsive hydrogel microstructures. As a proof of concept, a four-claw microgripper is fabricated, which is smaller than the most existing microrobots with both shape morphing and locomotion abilities and has higher magnetically driven locomotion speed. The feasibility of the microgripper for object delivery is also demonstrated. This work paves the way for the design of shape morphing microrobots with high magnetically driven locomotion performance that have potential applications for micro-object manipulation and minimally invasive surgery.

### 4. Experimental Section

**Materials:** Acrylic acid (AAc, 99%), *N*-isopropylacrylamide (NIPAAm, 98%), acrylamide (AAm, 99%), EL (98%), polyvinylpyrrolidone (PVP, average \( M_w \approx 1 \times 10^6 \)), *N,N*-dimethylformamide (DMF, 99.5%), *N,N*-methylenebisacrylamide (BIS, 99%), isopropanol (IPA, 98%), and

![Figure 7](image-url)
triethanolamine (TEA, 99%) were purchased from Aladdin Chemicals. Diphenyl-1,2,4-triazoline (DPEPA, 98%) was purchased from American Barki Chemical Inc. 4,4‘-bis(diethy lamino)benzophenone (EMK, 97%) was obtained from Reading Chemical Technology (Shanghai) Co. Ltd. 2,4,6-Trimethylbenzyldiphenyl phosphine oxide (TPO, 97%) was purchased from BASF. Fe$_3$O$_4$ NPs (PVP coating, 20 nm) were purchased from US Research Nanomaterials Inc. All chemicals were used directly as received.

**pH-Responsive Hydrogel Precursor:** The pH-responsive hydrogel precursor is prepared following a typical procedure.\(^{1,13}\) Functional monomers NIPAAm (1.6 g) and AcA (0.8 mL) were dissolved in EL (1 mL). Then, PVP (0.15 g) was added to adjust the hydrogel precursor viscosity, followed by stirring for 12 h when PVP was completely dissolved in EL. The aforementioned solution (2.5 mL), DPEPA (0.4 mL), TEA (0.5 mL), and EMK/DMF solution (100 μL, 20 wt%) were mixed and stirred for 2 h to ensure the complete component mixing.

**Magnetic NP-embedded hydrogel precursor:** The magnetic NP-embedded hydrogel precursor was prepared by dispersing a certain amount of Fe$_3$O$_4$ NPs in EL, followed by the same steps as preparing the pH-responsive hydrogel precursor. The magnetic NP-embedded hydrogel precursor was being constantly stirred to prevent Fe$_3$O$_4$ NPs from aggregating.

**PAAm Hydrogel Precursor:** In a typical procedure, 1.2 g AAm as monomer, 0.4 g BIS as cross-linker, 0.5 mL TEA as photosensitizer, and 100 μL TPO/DMF as photoinitiator (20 wt%) were added to 6 mL EL, which was being constantly stirred for 2 h to obtain a homogeneous hydrogel precursor.

**Fe$_3$O$_4$/EL Suspension:** Fe$_3$O$_4$/EL suspensions with concentrations of 5 and 15 mg mL$^{-1}$ were obtained by adding 25 and 75 mg Fe$_3$O$_4$ NPs in 5 mL EL, respectively. The suspensions were treated with ultrasound for 5 min. Then, let the suspension stand for 30 min at the room temperature to make sure that large particles deposited in the bottom of the bottle. The suspension without large particles was used for coating.

**Fabrication of Microrobots with Magnetic Surface Coating Structure:** A commercial two-photon DLW system (Nanoscribe GmbH, Germany) with a 63× oil immersion objective (numerical aperture of 1.4 from Zeiss) was used to fabricate the pH-responsive shape morphing hydrogel microstructures. The printing substrate (a 22 mm × 22 mm cover glass from Thermo Fisher Scientific Inc.) was cleaned by isopropanol rinsing and nitrogen purging before printing. Then the pH-responsive hydrogel precursor was dropped on the center of the substrate and then loaded into the two-photon DLW system. During printing, the laser power (0–50 mW) and scanning speed (0–100 mm s$^{-1}$) could be dynamically modulated. In this work, a laser power of 15 mW and a scan speed of 5 mm s$^{-1}$ were used to photopolymerize hydrogel with low degree of cross-linking, and a laser power of 40 mW and a scan speed of 5 mm s$^{-1}$ were used to photopolymerize hydrogel with high degree of cross-linking. After printing, the printed microstructures were developed by using isopropanol to excess unpolymerized precursor solution. The substrate was cut around the printed microstructures to fit the size of container and then completely put in a 10 mm × 10 mm × 6 mm container, after which 200 μL of 3 mg mL$^{-1}$ Fe$_3$O$_4$/EL suspension was dropped in the container. After EL completely evaporated, the Fe$_3$O$_4$ NPs were coated on the surface of the microrobots. To obtain microrobots with different thicknesses of Fe$_3$O$_4$ NPs coating, 200 μL of 15 mg mL$^{-1}$ Fe$_3$O$_4$/EL suspension, 400 μL of 15 mg mL$^{-1}$ Fe$_3$O$_4$/EL suspension, and 600 μL of 15 mg mL$^{-1}$ Fe$_3$O$_4$/EL suspension were added into the same size container. The PAAm hydrogel precursor was spin-coated on the surface of the microrobots at a speed of 1000 rpm for 20 s, and then exposed to UV light (365 nm) at 36 W (distance: ≈20 cm, time: 5 s). The fabricated shape morphing microrobots were removed from the glass substrate during their deformation and detach from the glass substrate when the environment changes, as shown in Figure S7, Supporting Information. Optical images of the fabricated microrobots were taken using a digital microscope (RH-2000, Hirox, Japan). SEM characterization was performed on a TESCAN-MAIA 3 GMU microscope.

**Magnetic Manipulation:** The locomotion velocities of the cuboid-shaped microrobots and the microgrippers were measured under a uniform rotating magnetic field, which was generated by a commercial magnetic manipulation system (MFG-100, MagnebotiX AG, Switzerland). A top-view camera was used for observations and recording videos of the locomotion. All the experiments were performed on the surface of a clean glass in an aqueous solution.

The feasibility of the microgripper for object delivery was examined by using a permanent magnet. We used a magnet to guide the movement of the microgripper from one place to the other by manually manipulating the magnet to change its position and orientation.

**Cell Culture:** The L929 cells were cultured on the printed hydrogel microstructures with and without Fe$_3$O$_4$ NPs coating to evaluate the cytotoxicity of the samples. Before cells culturing, the printed hydrogel microstructures with and without Fe$_3$O$_4$ NPs coating were soaked in water for 24 h, and the water was changed every 3 h. L929 fibroblast cells were cultured with complete RPMI medium 1640 (Giboc) containing 10% fetal bovine serum (Giboc) and 1% penicillin/streptomycin solution (Giboc) in a 5% CO$_2$ incubator at 37°C. The cells were treated with trypsin-EDTA (Giboc) and resuspended with complete RPMI medium 1640. The cells with a density of 1 × 10$^4$ were seeded onto the printed hydrogel structures and allowed to grow for 24 h. The cytocompatibility of the printed hydrogel structures and Fe$_3$O$_4$ NPs was analyzed by Live/Dead assay. Calcein AM (2 μM) (in DPBS) and 4 μM EthD-1 (Invitrogen) working solution were added to petri dish after the dish was washed with DPBS (Giboc). The petri dish was then incubated in a 5% CO$_2$ incubator at 37°C for 20 min. A fluorescence microscope (Olympus IX71) was used to observe the morphologies of the cells.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

enhanced locomotion, magnetic microrobots, shape morphing, surface coating structures
