Template-assisted electroforming of fully hard-magnetic helical microactuators

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Abstract

We report on the fabrication of semi-hard-magnetic microhelices using template-assisted electroforming. The method consists of electrodepositing a material on a sacrificial mandrel on which a pattern has been previously written. To electroform the helical microswimmers, a helical template on a polymer-coated metallic mandrel is created using a laser, which precisely ablates the polymer coating and exposes the mandrel surface. Subsequently, the semi-hard-magnetic material is electrodeposited in the trenches produced by the laser. In this investigation, the helical structures are obtained from an electrolyte, which enables the production of hard-magnetic CoPt alloys. We also show that electroformed semi-hard-magnetic helical microswimmers can propel in viscous environments such as silicon oil in three dimensions and against gravity. Our manufacturing approach can be used for the fabrication of more complex architectures for a wide range of applications and can be potentially extended to any electroplatable material.
1. Introduction

Electrochemical deposition and processing techniques, such as electrodeposition, electroless or galvanic displacement, have become key for manufacturing micro- and nanocomponents in electronic devices and magnetic systems.[1] These methods have greatly contributed to a variety of research areas as they allow manufacturing complex shapes with a variety of composition and size.[2] The field of small-scale robots is a research area that has particularly benefited from electrochemical manufacturing technologies. In the review “Nano/Microrobots Meet Electrochemistry”,[3] the versatile role of electrochemical methods in the production of micro- and nanorobots has been highlighted. Small-scale robots, also known as micro- and nanomachines, are tiny devices capable of locomotion in liquids fueled by chemicals spread in their surroundings[4] or powered by means of external energy sources.[5] Each locomotion strategy requires these machines to be built with specific materials. Nanowires,[6] nanotubes,[7] hinged nanorods,[8] Janus microparticles[9] and small-scale porous microarchitectures[10] are a few examples of electrochemically synthesized building blocks that have been used for manufacturing micro- and nanorobotic platforms.

One of the more common configurations of micro- and nanorobotic platforms is the helical shape. These structures, which usually contain magnetic material in their body, are propelled by means of rotating magnetic fields converting rotational motion into translational corkscrew motion.[11] This locomotion strategy is inspired by the motility mechanism of certain microorganisms such as E. coli, which rotate their flagella to propel their bodies. For this reason, helical small-scale swimmers are also known as artificial bacterial flagella (ABFs). Since the first reported microscale ABFs
developed by Nelson and co-workers in 2007,[12] a number of helical swimmer designs have been realized by exploiting different fabrication strategies. Electrochemical fabrication techniques have also been used for the production of helical micro- and nanomachines. Microscale magnetic ABFs have been fabricated using helically assembled phospholipids as scaffolds, subsequently coated with a magnetic alloy by means of electroless deposition.[13] Template-assisted electrodeposition has been utilized to fabricate hybrid micrometric ABFs in three-dimensional arrays obtained by two-photon polymerization.[14] Combining template-assisted electrodeposition in nanoporous anodized aluminum oxide arrays with dealloying and chemical vapor deposition, nanoscale ABFs have also been reported.[15]

In previous reports, four different approaches have been identified for achieving the corkscrew motion mechanism in micro- and nanohelices as depicted in Figure 1. The first strategy consists of attaching a magnetic head exhibiting shape anisotropy to a helical tail. This method presents more challenges in terms of fabrication, as more steps are involved to fabricate each component. For example, swimmers of this configuration were fabricated by combining photolithography, molecular beam epitaxy, and e-beam evaporation.[12] Another option is to form helices by electrodeposition in 3D templates obtained by two-photon polymerization.[14] This is an attractive method due to the wide choice of platable materials and conditions. However, electrocrystallization incompatibilities[16] and issues such as hydrogen evolution or damage of the photoresist caused by local variations of pH may dramatically affect the structure and the properties of the device.
The second way to build magnetic helical devices involves forming the helical bodies by means of 3D photolithography\cite{17} or glancing angle deposition,\cite{18} and subsequently coating them by depositing magnetic material using chemical vapor deposition or sputtering. In this case, tailoring the composition of the magnetic material is usually difficult, as it requires using targets with different ratios of elements or components. Additionally, the amount of magnetic material to be deposited is limited, and this may be detrimental for their magnetic manipulation. Note that magnetic forces and torques are proportional to the magnetic volume of the material.

The third method involves fabricating helical microstructures from polymer composites containing magnetic nanoparticles (NPs). To achieve corkscrew locomotion it is important that the NPs are oriented perpendicular to the long axis of the helix.\cite{19} This approach exploits the concept of programming the shape anisotropy, which consists of pre-defining the easy magnetization axis in a specific shape.\cite{20} While this is an attractive approach, the method is limited by the volume of particles that can be hosted in the matrix without compromising its mechanical stability or its photocurability.\cite{21}

The fourth approach consists of creating helical devices made of \textbf{hard- or semi-hard magnetic material}. Capitalizing on their magnetic memory effects, microstructures with \textbf{hard-magnetic characteristics} such as helices or tubes can be permanently magnetized in the direction perpendicular to their axis provided that they exhibit sufficient remanence.\cite{22} This approach is not only attractive from the point of view of manufacturing, but also regarding the forces and torques that can be exerted to the
devices, as they are proportional to the magnetic volume. To date, no magnetic microhelix has been fabricated entirely out of hard-magnetic material.

In this paper, we exploit the electrochemical technique electroforming to fabricate microscale ABFs fully made of a semi-hard-magnetic cobalt-platinum alloy. Electroforming has been successfully used to fabricate soft-magnetic tubular microrobots for ophthalmic drug delivery.\[^{23}\] The method reported here exploits the concept of template-assisted electroforming on sacrificial filament mandrels and can be extended to the fabrication of a wide number of electroplatable materials. To electroform the helical microswimmers, a template on a self-curing polymer-coated metallic mandrel is created using a laser, which precisely ablates the coating and exposes the mandrel surface. Subsequently, the semi-hard-magnetic material is electrodeposited in the trenches produced by the laser. In this investigation, we have chosen CoPt as the material to fabricate the helical structures, due to its hard-magnetic properties.\[^{24}\] We also show that electroformed semi-hard-magnetic helical microswimmers can propel in three dimensions in viscous environments such as silicon oil. Our results pave the way to the realization of fully hard-magnetic untethered microswimmers for a variety of microrobotic applications.

2. Experimental Section

Aluminum (Al) wires of 250 μm diameter were thoroughly cleaned with acetone, isopropanol, and deionized water. A micromanipulator, Sutter Instrument® MP-285, was used to dip-coat the Al wires in a self-curing polymer. The Al wires were dip coated five times at intervals of 3 min, at a constant dipping speed of 4 mm/s, forming an isolating layer. The polymer at the endings of the Al wires was removed with
acetone and an approximately 25-mm long polymer layer in the center of the wire was left to dry. The polymer-coated Al wires were mounted into a custom-built setup to hold the wire. The coating was then patterned by laser ablation while rotating the wire (see more details and Figure S1 in supporting information).

To achieve a complete and homogenous CoPt electrodeposition, the passivated aluminum-oxide layers on the ablated trenches were removed by dipping the Al wires in a potassium hydroxide (KOH) etchant solution (0.5 M) for 50 s. The etched surface was then immediately activated by submerging the wire in a palladium(II) chloride solution for 50 s. The activated helical trenches were then coated with a gold seed layer using electroless deposition (Transene Inc.) at 90°C for 25 min. The subsequent electrodeposition of CoPt was performed in a thermostatted one-compartment two-electrode cell filled with 100 ml of an electrolyte (table S1) containing platinum and cobalt salts. The composition of this electrolyte was slightly modified with respect to a previously reported formulation.\textsuperscript{[25]} The electrodeposition was performed with a PGSTAT302N Autolab potentiostat/galvanostat. The helical structures were deposited galvanostatically at a current density of –20 mA cm\textsuperscript{−2}. The CoPt electrolyte was operated at a temperature of 65 °C, a pH of 8.5, and at quiescent conditions. A platinum-coated titanium mesh of 2.5 x 2.5 cm acted as the counter electrode. The volume of the electrolyte in the cell and the pH of the bath were monitored at the beginning and at the end of each deposition and adjusted with deionized water and NaOH, if necessary. The morphology and composition of the helices were evaluated using a FAI Quanta 200 Scanning Electron Microscope (SEM) and energy dispersive X-ray (EDX) spectroscopy, respectively. The elementary quantification was performed using K lines at 20 kV. The magnetic properties of the helical microstructures were characterized using a Vibrating Sample Magnetometer (VSM)
MicroSense EZ9. After deposition, the helical microstructures were carefully washed. The polymer template was removed with acetone. Pre-magnetization of the helical structures (still supported on the mandrel) was performed using the VSM by applying a field of 2.2 T. The helices were pre-magnetized perpendicular to their long axis. The Al wires were then etched in 1 M KOH for approximately two hours. The fabrication process is schematically shown in Figure 2a.

3. Results and Discussion

In order to successfully electrodeposit any material on the templated mandrel, the process parameters of the laser must be optimized when writing the pattern in order to ablate only the polymer layer and not the Al wire underneath. Figure S2 shows the Al wire with an ablated motif obtained with optimized parameters, and the motif selectively plated with gold using electroless deposition (see supporting information).

Figure 2b-c show SEM images of successfully electroformed microscale CoPt ABFs. The ABF shown was 1.5 mm in length, with a fairly constant diameter of 250 µm and a cross-section of approximately 8.5 µm by 128 µm. The morphology at the edges of the helices appeared rougher probably due to the local increase of the current density. Special care had to be taken to remove the helices due to their mechanical fragility. Importantly, the etching of the aluminum mandrel had to be performed slowly in solutions of KOH not exceeding a concentration of 1 M. Higher concentrations led to violent generation of bubbles that damaged the helical structure. The helix exhibited a composition of 83 wt% of Co and 16 wt% of Pt. Very small amounts of P were detected (around 0.2 wt%) due to the presence of sodium hypophosphite in the electrolyte. While this amount is rather small, P accumulates at the grain boundaries
blocking the movement of domain walls, consequently enhancing the hard-magnetic properties of CoPt alloys.\textsuperscript{[26]}

Figure 3 shows a normalized hysteresis loop from a helix exhibiting a $H_c(\perp) = 1150$ Oe and a perpendicular squareness of $S(\perp) = 0.3014$. $S(\perp)$ is the ratio of $M_r(\perp)/M_s$ where $M_r(\perp)$ is the remanence after magnetizing the helical structure perpendicularly to its long axis, and $M_s$, the saturation magnetization. The maximum magnetic moment that the helix can exhibit is $m_S = 8.69 \times 10^{-6} \text{ A} \cdot \text{m}^2$ at an applied magnetic field of $2.2 \times 10^4$ Oe. The magnetic properties exhibited by the semi-hard-magnetic helix were sufficient for a successful pre-magnetization of the structure in the perpendicular direction of the helical axis and its further magnetic manipulation.

The principle for the magnetic actuation of a magnetic helix is based on the magnetic torque $T$ generated upon the application of an applied magnetic field $H$, which is given by the following expression:

$$T = \mu_0 m \times H \text{ (1)}$$

where $m$ (A$\cdot$m$^2$) and $H$ (A$\cdot$m$^{-1}$) are the magnetic moment and the magnetic field, respectively, and $\mu_0$ is the magnetic permeability constant. When a magnetic object is subject to an external magnetic field, the object experiences a torque that causes the object to rotate and align its easy magnetization axis with the direction of the applied magnetic field. As the object is aligned, the torque disappears. To achieve a continuous rotation of the object, the magnetic field has to be rotated. When applying this rotating field to a helix, which is perpendicularly magnetized (Figure 3b-ii and video S1), rotation around the long axis of the helix and consequent translational
motion are expected (Figure 3b-iii and video S2). Considering that the helix is manipulated at a very low field of 20 mT, the magnetic moment of the helix is close to the magnetic moment at remanence $m_r$, so the experienced torque was calculated to be $5.24 \times 10^{-5} \text{ N} \cdot \text{m}$.

Our hard-magnetic helices were tested in a 5-degree-of-freedom electromagnetic system (Octomag from Magnebotix AG)\cite{27} and were manipulated in a cubic pool (15.625 cm$^3$) containing highly viscous silicone oil exhibiting a viscosity of $\eta = 1000 \text{ Pa} \cdot \text{s}$. A magnetic field of 20 mT with a rotation frequency of 3.1 Hz was applied. As can be seen in Figure 3c, the helix was able to perform corkscrew motion in a pre-defined trajectory in three dimensions. The inset in Figure 3c shows the top view. Figure 3d shows how the helix can successfully swim against the gravity.

4. Conclusions

Microscale hard-magnetic microswimmers were successfully fabricated for the first time by template-assisted electroforming of a CoPt alloy on sacrificial mandrels. They were successfully propelled in three dimensions by rotating magnetic fields in highly viscous fluids. The fabrication of complex-shaped fully hard-magnetic structures is an important step for the development of magnetically powered devices and can be extended for the manufacturing of microtools and microdevices not limited to biomedical applications.
Acknowledgements

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6. References


Fig. 1. Types of magnetic ABFs: (a) ABF with a soft-magnetic head and non-magnetic tail. (b) ABF with ferromagnetic thin coating. (c) ABF of a superparamagnetic nano composite. (d) ABF of ferromagnetic material.
Fig. 2. (a) Fabrication sequence of ABFs, i) coating the Al wire with an isolating polymer, ii) patterning the isolation polymer, iii) electroless gold coating the trenches, iv) electrodeposition of the ferromagnetic material, v) removal of the isolation polymer, vi) Al etching and perpendicular magnetization of the ABF. (b) and (c) SEM images of hard-magnetic CoPt ABFs electrodeposited at −20 mA cm⁻².
Fig. 3. (a) Magnetic hysteresis loop of a CoPt ABF (measured along the helix short axis) showing the hysteresis behavior typical of a hard-magnetic material. (b) Actuation principle of the ABF. Side view and top view (insets) of the 3D magnetic manipulation under rotating magnetic fields of the hard-magnetic ABF in silicon oil: (c) moving in all the three dimensions; and (d) swimming against the gravity.
Supporting information

Template-assisted electroforming of fully hard-magnetic helical microactuators

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Custom built-setup for the fabrication of templated mandrels

Figure S1. Custom setup to hold and rotate the wire while patterning the helix.

The polymer-coated Al wires were mounted into a custom-built setup to hold the wire (Figure S1) and to allow a concentric rotation. Albrecht chucks were used to hold the wires on both sides. One of the shafts used to clamp a chuck could be adjusted back and forth to control the tension on the wire. This was crucial to keep the wire straight, as any eccentricity could lead to periodic defects in the ablation pattern. Most of the parts of the setup were designed using Siemens NX and 3D printed. Standard parts such as roll bearings and cogwheels were bought from Maedler GmbH. The shafts and the distance holders, which provided stability and alignment, were CNC machined. A Maxon motor provided the rotation of the wire. The cured polymer layer was then ablated along its length (2 mm) with a pitch angle of 27° by a LaserMill.
from New Wave Research with an incident UV laser of 20 Hz pulse, laser intensity of approximately 0.68 J cm$^{-2}$ with a beam width of 80 μm while rotating the Al wire at 1.53 rpm. In order to calculate the total area $A$ of the ablated trench the following equation was used:

$$A = s \cdot L$$

where $s$ corresponds to the laser spot size, and $L$ to the length of the expanded helix. $L$ is given by the following formula:

$$L = 2\pi \cdot \frac{d}{2} \sqrt{1 + (\tan \alpha)^2 \cdot t}$$

where $d$ is the wire diameter, $\alpha$ is the pitch angle, and $t$ is the number of turns. The pitch angle $\alpha$ depends the laser speed $v_L$, the rotation of the wire $f$, and the wire diameter $d$ as follows:

$$\alpha = \arctan \left( \frac{v_L}{2\pi \cdot f \cdot \frac{d}{2}} \right)$$

Figure S2. a) optical images of the wire, i) after patterning the isolation polymer, ii) after electroless gold deposition, iii) after electroforming with CoPt. b) Optical image of an ABF. c) SEM images of an ABF.
The process parameters of the laser must be optimized when writing the pattern in order to ablate only the polymer layer and not the Al wire underneath. Figure S2ai-iii show the Al wire with an ablated motif obtained with optimized parameters and the motif selectively plated with gold using electroless deposition. Figure S2b shows an optical image of the ABF and Figure S2c SEM image of the microscale metallic ABF.

**Composition of the electrolyte**

The electrolyte contains diamminedinitritoplatinum(II) and cobalt(II) sulphamate (Co(NH₂SO₃)₂) as metal salts. Ammonium citrate ((NH₄)₂C₆H₆O₇) and glycine (NH₂CH₂COOH) were the complexing agents. Sodium hypophosphite (NaH₂PO₂·H₂O) was used as a magnetic hardener. Sodium saccharinate (C₇H₄NNaO₃S) acted as stress reducer.

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>Concentration / mol 1⁻¹</th>
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<tr>
<td>Pt(NO₂)₂(NH₃)₂</td>
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</tr>
<tr>
<td>Co(NH₂SO₃)₂</td>
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</tr>
<tr>
<td>(NH₄)₂C₆H₆O₇</td>
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<tr>
<td>NH₂CH₂COOH</td>
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<tr>
<td>NaH₂PO₂·H₂O</td>
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<tr>
<td>C₇H₄NNaO₃S</td>
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