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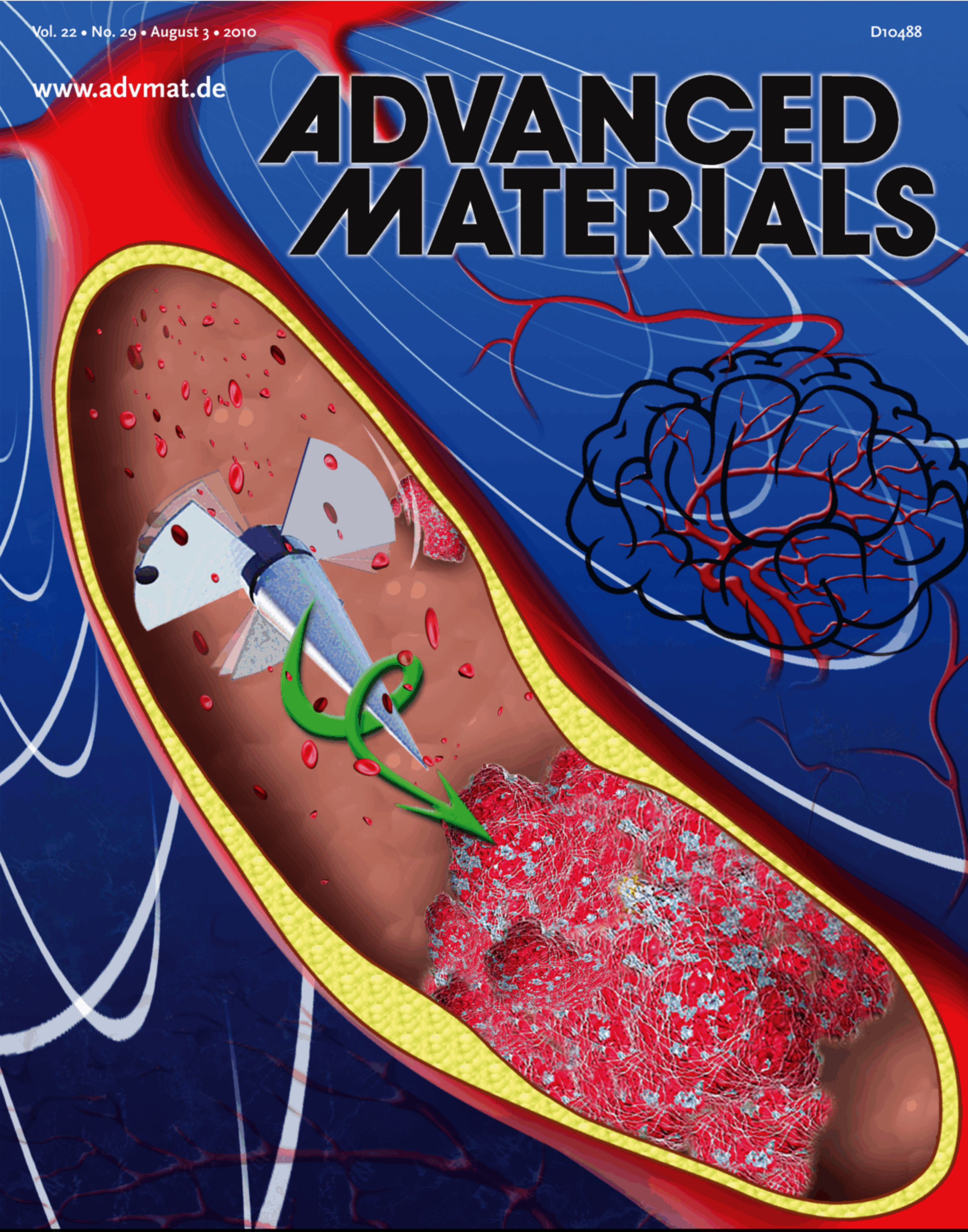

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Remote-Control Nanomachines

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Ferrofluids for Fabrication of Remotely Controllable Micro-Nanomachines by Two-Photon Polymerization

By *Hong Xia, Juan Wang, Ye Tian, Qi-Dai Chen,* Xiao-Bo Du, Yong-Lai Zhang, Yan He,* and *Hong-Bo Sun**

Miniaturized smart machines with micro-nanometer sized moving parts have now been utilized for on-site, in vivo sensing, monitoring, analysis and treatment in narrow enclosure, harsh environment, and even inside human body.[1–10] Despite the fact that a vast majority of currently available micromachines are produced with silicon by lithography, represented by Si: MEMS (silicon microelectromechanical systems) technique, a recent trend of the field resorts to polymers.[11] As a designable three-dimensional micro-nanoprocessing method, two-photon photopolymerization (TPP) of photopolymers provides a novel route for fabricating micro-nanomechines with higher spatial resolution and smaller size.[12–14] However, introduction of driven force to these tiny devices for precise micro-manipulation constitutes the main problem for the advanced applications of these micro-nanomachines, for example, remote control is indispensable for intelligent micromachine that may be placed in blood vessels for health care. It is therefore of great importance to find novel fabricative and driven techniques for making functional micronanomachines with precise motion control.

Magnetic force drive technique which has been widely applied in macroscopical instruments would be an ideal method for remote control due to its simple, mind, safe and non-contact properties.[15–18] However, up to now, magnetic force is still not properly applied to remote control of micro-nanomachines for accomplishing desired task. Possible reason for this gap would be the lack of nanotechnology of appending magnetic components to existing micro-nanomachines, or to photopolymer precursors for laser fabrication. Generally, magnetic components such as nanoparticles which usually behave inorganic properties are really difficult to be introduced into polymeric carriers in a highly dispersed, largely doped fashion without significant phase separation.[19] If magnetic nanomaterials can be homogeneously, largely and stably embedded in photopolymerizable resin through a simple method, magnetic force controllable micro-nanomachines would be fabricated accordingly.

[*] H. Xia, J. Wang, Y. Tian, Q. D. Chen, Y. L. Zhang, Y. He, Prof. H. B. Sun
State Key Laboratory on Integrated Optoelectronics
College of Electronic Science and Engineering
Jilin University
2699 Qianjin Street, Changchun,130012 (People's Republic of China)
E-mail: hbsun@jlu.edu.cn; chenqd@jlu.edu.cn
Dr. X. B. Du
College of Physics
Jilin University
119 Jiefang Road, Changchun, 130023 (People's Republic of China)

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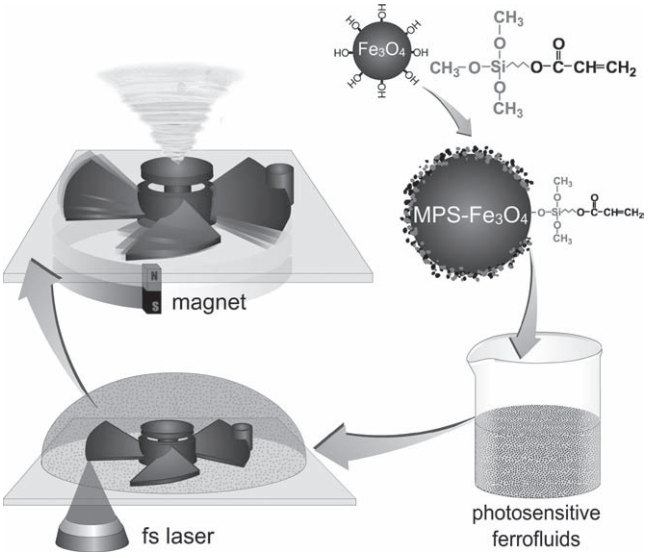
Herein, we demonstrate a design and fabrication of remote-controllable micromachines by femtosecond laser induced two-photon polymerization of stable, homogeneous and transparent ferrofluids resin composed of methacrylate groups modified Fe_3O_4 nanoparticles and photoresists. As two typical models, a micro-spring and a micro-turbine were successfully fabricated for remote control under additional magnetic force. The development of remotely controllable micro-nanomachines would shorten the distance between actionless micro-nanostructures and smart micronanorobots.

Scheme 1 illustrates the schematic procedures for fabrication and remote control of our micromachines. Firstly, Fe_3O_4 nanoparticles were synthesized according to the literature.[20] In order to embed these magnetic nanoparticles into the photoresists homogeneously, surface of the as-synthesized Fe_3O_4 nanoparticles was chemically modified by 3-(trimethoxysilyl)propyl methacrylate (MPS), which would impart dispersible and photopolymerizable properties to these magnetic nanoparticles. Transmission electron microscope (TEM) image (**Figure 1a**) shows the size of the nanoparticles is around 10 nm. Wide angle X-ray diffraction (XRD) pattern (Figure 1b) exhibits a series of diffraction peaks in 2θ region of 20°–70° in surface modified Fe_3O_4 nanoparticles. The whole set of peaks could be assigned to 220, 311, 400, 422, 511 and 440 planes of cubic inverse spinel structured Fe_3O_4, and there is not any impure phase was observed from the pattern. Furthermore, FT-IR spectrum gives strong evidence of the presence of silane and organic groups on the surface of Fe_3O_4 nanoparticles, indicating the successful grafting of MPS groups (Figure 1c). Subsequently, the MPS-Fe_3O_4 nanoparticles were homogeneously doped into our photoresists, which was composed of methyl acrylate (MA, 37.14 wt%) as monomers, pentaerythritol triacrylate (PETA, 60.00 wt%) as crosslinkers, benzyl (BZ, 1.66 wt%) as photoinitiators, and 2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl) butan-1-one (BAMPB, 1.20 wt%) as photosensitizers. The above precursor was used for femtosecond laser prototyping of various micro-nanomachines.

Before laser processing, the magnetic property of MPS-Fe_3O_4 nanoparticles and their photoresist nanocomposites are experimentally characterized. As seen from vibrating sample ferromagnetometry (VSM, **Figure 2a**), remanence and coercivity could hardly be observed, indicating the superparamagnetism of the MPS-Fe_3O_4 particles. After doping the MPS-Fe_3O_4 nanoparticles into the photoresists, a flaxen-transparent hybrid is obtained which is very uniform and stable. Even under gravitation, the magnetic nanoparticles are still homogeneously dispersed without separation from organic liquid carrier, indicating a stable colloidal dispersion of photopolymerizable resin



Scheme 1. Fabricative procedures of remotely controllable micro-nanomachines.

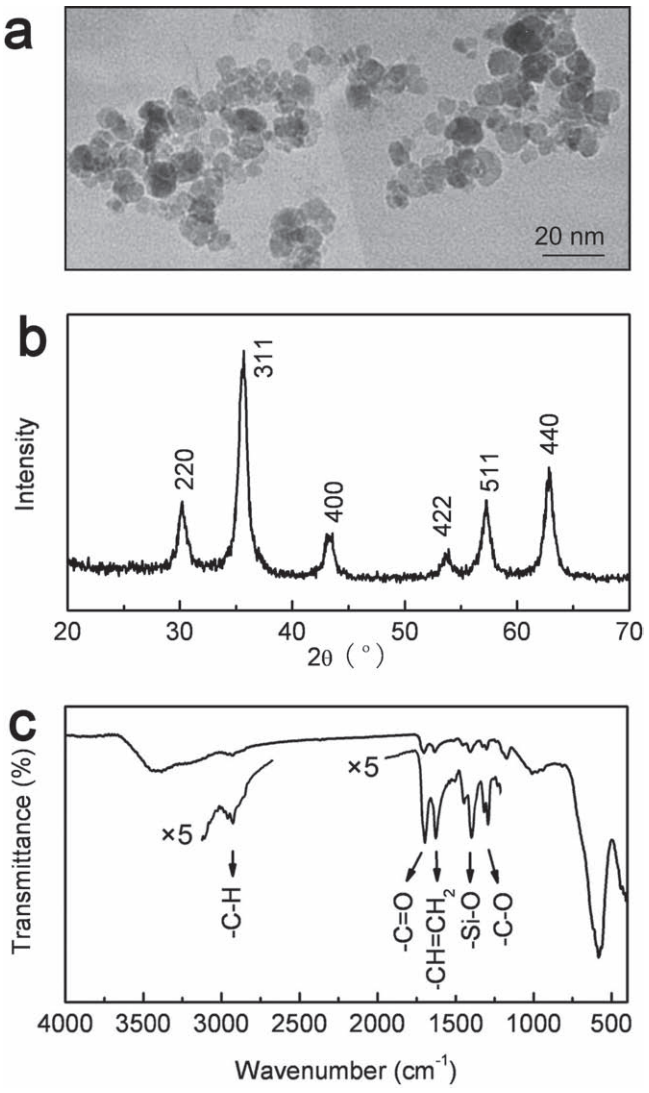


Figure 1. Characterizations of MPS-Fe_3O_4 nanoparticles. a) TEM image of MPS-Fe_3O_4 nanoparticles. b) XRD pattern of MPS-Fe_3O_4 nanoparticles. c) FT-IR spectrum of MPS-Fe_3O_4 nanoparticles.

and MPS-Fe_3O_4 nanoparticles, i.e. ferrofluid was obtained (Figure 2b). Flow property of as-synthesized ferrofluid (2.1 wt% of MPS-Fe_3O_4) under magnetic field was further characterized. As shown in Figure 2c, at the shear rate of 0.1 S^{-1} and 50 S^{-1}, shear stress of the sample increases with the intensities of extra magnetic field, indicating their obvious magneto-rheological activities. Relationship between viscosity and shear rate under magnetic field intensity of 0.43T reveals that bingham model was suitable for characterizing its inherent flowing property (Figure 2). The above results confirm the homogeneous and stable features of our ferrofluid. Herein, the acrylic groups presented in both MPS-Fe_3O_4 nanoparticles and polymeric precursor (monomer and crosslinker) impart chemical consistency and physical dispersancy to this organic/inorganic hybrids due to compatibility and similitude principle. It is worthy pointing out that the transparent, homogeneous and photopolymerizable features of these ferrofluids contribute the possibility of following laser processing.

In our experiments, stable ferrofluids was successfully prepared in a wide range of MPS-Fe_3O_4 content (0.5–20.0 wt%). Agglomeration of the magnetic particles would occur when more than 20 wt% of MPS-Fe_3O_4 was mixed into the ferrofluids. Herein, a ferrofluid containing 2.1 wt% of MPS-Fe_3O_4 was chosen as a representative example for micro-nanoprocessing. A drop of above-mentioned ferrofluid on a glass wafer was pinpointly written according to computer programs by 790-nm Ti-sapphire laser with 120-fs pulse duration and 80-MHz repetition rate from a mode-locked. The laser beam was tightly focused by a ×100 oil immersion objective lens with a high numerical aperture NA = 1.45. The focal spot of the laser beam was scanned laterally by steering a two-galvano-mirror set, and was vertically moved along the optical axis by a piezo stage. The linear absorption of the black Fe_3O_4 requires an increased threshold of two-photon photopolymerization of the resin. Therefore, 5–7mW laser power measured before the objective lens, 50-nm scanning step length and 600-μs exposure duration of each voxel are adopted. After fabrication, the entire structure was rinsed with ethanol for 5 minutes to remove unpolymerized resin, and a solidified micro-nanomachine was finally obtained. For further operation, the macro-machines were immersed in acetone which was used as a liquid media. In fact, PH standard buffer solutions or other organic solvents like methanol and ethanol are also suitable for remote control of the spring without any difference, which indicates a general applicability of our micro-machine under different conditions.

Figure 3 shows optical microscopy images of a micro-spring during its movement process. As illustrated in the schematic model (Figure 3a), one end of the spring is fixed to a polymerized cubic anchor attached to the substrate, and the other end is polymerized into a sphere shape as a moving part. In our case, the spring structure was immersed into a solvent and placed under an optical microscope. The MPS-Fe_3O_4 nanoparticles as magnetic dipoles were homogeneously incorporated in both

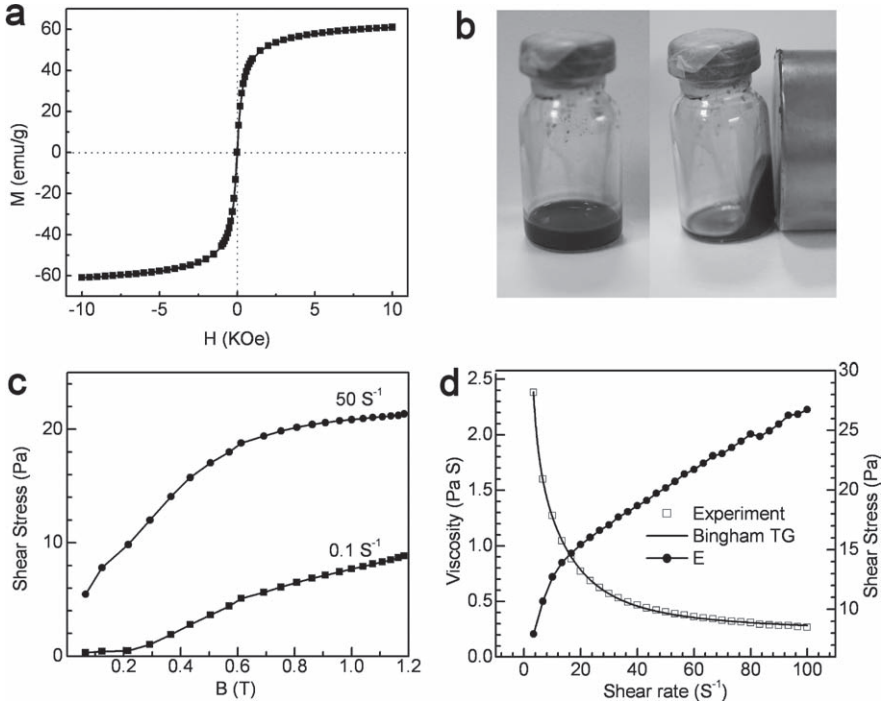


Figure 2. a) VSM spectrum of the MPS-Fe_3O_4. b) Photographs of static ferrofluid and the ferrofluid under magnetic force. c) Shear stress curves of the ferrofluid as a function of magnetic field intensity at the shear rate of 0.1 S^{-1} and 50 S^{-1}. d) Viscosity and shear stress curves of the ferrofluid as a function of the shear rate under the magnetic field intensity of 0.43 T.

driven part (bead) and spring structure, thus the micro-spring would give response to the stimulin of external magnetic field gradient. When a ferromagnet approached the bead along the axis direction of spring, the elongation and reversion progress of the spring could be observed by the microscope clearly. Figure 3b–f show a sequence of frames of this process. The original length of the micro-spring is 60 μm (Figure 3b). During its elongation, length values of 81 μm (Figure 3c), and 86 μm (maximum, Figure 3d) were observed. It is of interest to note that different cycles of the micro-spring exhibit different elongation ratio along the axis direction (see the blue arrow). Proposed reason for this phenomenon was explained as the magnetic force acted on the spring itself due to its non-ignorable mass compared with the driven bead. (for detailed discussion, see supplementary information) After removal of the ferromagnet, the elongation value reduced to 75 μm (Figure 3e), and finally reverted to original length (Figure 3f). Moreover, the bead of micro-spring could also be driven to perform a right-and-left sway movement. As shown in Figure 3g–l, different slope angle of the micro-spring was recorded. Based on above results, it is reasonable to conclude that our micro-spring is very flexible and controllable, which would be generally adequate for multiform manipulation.

The fabrication and remote control of micro-nanomachines are not only limited to micro-spring, a micro-turbine was also developed for remote control. As shown in **Figure 4**, a collar-joint micro-turbine was successfully created according to the pre-designed model (Figure 4a). The micro-turbine was about 35 μm in diameter with a central axletree and three blades. For magnetic control, a piece of ferromagnet was placed on a vortical device around the micro-turbine (Figure S1). It could be clearly observed form the supporting video (Supprting Information) that the micro-turbine rotated with an average rate of 3 revolutions per second. In our case, the rotating rate could be adjusted easily in the range of 0–6 rps. The development of micro-turbine represents another exemplar for remote control of micro-nanomachines, and it is believable that our micro-turbine would be of considerable interest in microfluidic field.

In conclusion, in order to fabricate smart micro-nanomachines with micro-manipulation feature, we have prepared a photopolymerizable ferrofluid for two-photo polymerization towards functional micro-machines. As typical examples, micrometer-sized spring and turbine was successfully created for magnetic force remote control. By using an external magnet, both of the two micro-machines could be easily manipulated to perform desired task. The combination of photopolymerizable ferrofluid resin and laser processing technology would make a

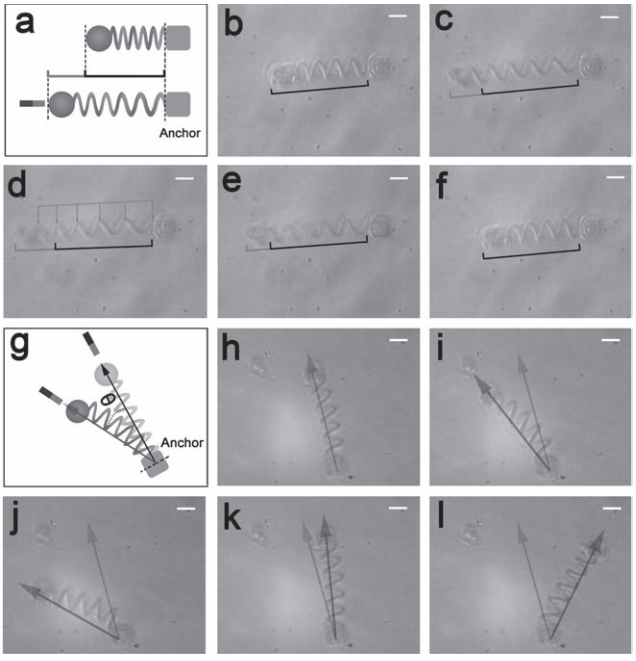


Figure 3. Remote control of the micro-spring in acetone. a–f) Elongation movement. a) Scheme model for elongation of the micro-spring. b) Original length of the microspring. c–e) Micro-spring with various elongations; f) recovery of the micro-spring; g–l) sway movement; g) scheme model for sway movement of the micro-spring; h–l) micro-spring with different slope angles. Scale bar, 10 μm. A piece of magnet with surface magnetic field strength of 1800 Gs is used for remote control of the micro-spring.

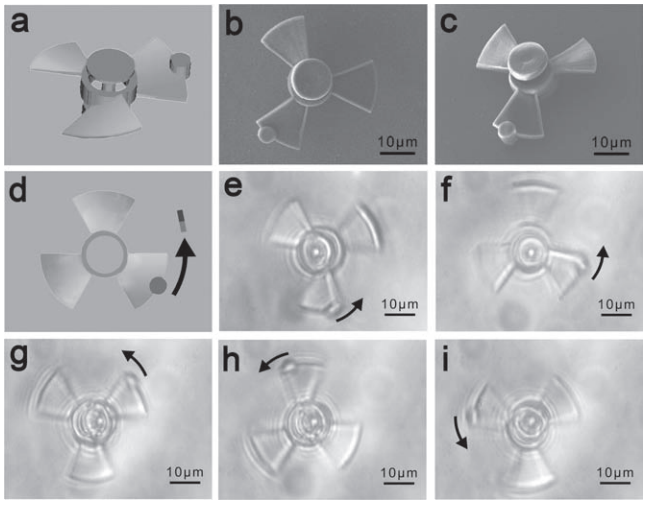


Figure 4. Remote control of the micro-turbine in acetone. a, model of the micro-turbine. b,c) SEM images of the micro-turbine. d) top view scheme model for circumgyratetion. e–i) optical microscopy images of the micro-turbine in a circumgyratetion cycle. For remote control and observation of the micro-turbine, a piece of ferromagnet was placed on a vortical device around the objective lens (Figure S1).

breakthrough in nanotechnology for easy fabrication and remote control of micro-nanomachines in a broad range of applications.

Experimental Section

Preparation of MSP-Fe_3O_4 Nanoparticles: Fe_3O_4 nanoparticles are synthesized according to the reported reference.[20] For further grafting, the Fe_3O_4 particle cores were mixed with ethanol (200 ml) in a flask, then surfactant MPS (1.22 g) was drop-wise added. The mixture was stirred for 24 h at room temperature and for 1 h at 80°C under Ar protection, respectively. After that, the powder was centrifuged and washed with ethanol for three times to remove excess MPS absorbed on the particles, giving MSP-Fe_3O_4 nanoparticles.

Preparation of Ferrofluid: A desired amount of as-synthesized MSP-Fe_3O_4 nanoparticles were added the the mixture of methyl acrylate (MA, 37.14 wt%), pentaerythritol triacrylate (PETA, 60.00 wt%), benzyl (BZ, 1.66 wt%), and 2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl) butan-1-one (BAMPB, 1.20 wt%). In our experiment, the content of MSP-Fe_3O_4 nanoparticles was in the range of 0 to 20wt%.

Fabrication of Micro-machines: As a typical fabrication, the ferrofluid-resin containing 2.0 wt% of MPS-Fe_3O_4 was pinpointly written according to computer programs by 790-nm Ti-sapphire laser with 120-fs pulse duration and 80-MHz repetition rate from a mode-locked. The laser beam was tightly focused by a ×100 oil immersion objective lens with a high numerical aperture NA = 1.45, and the focal spot was scanned laterally by steering a two-galvano-mirror set and along the optical axis by a piezo stage. 5–7mW laser power measured before the objective lens, 50-nm scanning step length and 600-μs exposure duration of each voxel are adopted. After fabrication, the entire structure was rinsed with ethanol for 5 min to remove unpolymerized resin.

Characterization: Transmission electron microscope (TEM) images were obtained from a Hitachi H-8100 microscope with accelerative voltage of 200 kV. Scanning electron microscope (SEM) images were obtained from a Jeol-7500F microscope. FT-IR spectra were performed on a Nicolet 6700 infrared spectrometer. X-ray diffraction patterns (XRD) were obtained with a Tokyo diffractometer using Cu-Kα radiation with wavelength of k = 1.5405 Å. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM). Flow property the ferrofluid was measure by MCR301 rheometer (ANTON-PAAR). Optical microscope images were obtained from a Motic BE400 microscope.

Supporting Information

Supporting Information is available online from Wiley InterScience or from the author.

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