Remote manipulation of micronanomachines containing magnetic nanoparticles

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We report remote manipulation of micronanomachines containing magnetic nanoparticles. Surface-modified Fe₃O₄ nanocrystals were synthesized as doping agents of the photopolymerizable resin, which was pinpoint written by femtosecond laser-induced two-photon photopolymerization to create microsprings. Owing to the nature of superparamagnetism of Fe₃O₄ nanoparticles, force exerted to the microsprings relies sensitively on the field gradient of the external ferromagnet, and various motions like elongation, bending, and swing are achieved in a well-controllable remote manner. As a noncontact, sensitive, easy, and environmentally friendly approach, the magnetic driving of micronanomachines may play an important role for nano and biological applications. © 2009 Optical Society of America

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Laser micronanofabrication technology [1,2] has been recently growing as one of the most promising approaches for the fabrication of microoptical components, micronanomachines, and their integrated systems [3,4]. The reasonably high spatial resolution and three-dimensional (3D) processing capability [5] make it possible to rapidly prototype complicated 3D structures like photonic crystals [6,7], binary lenses and mirrors [8], micro-oscillators, and rotators [3,9]. The method is particularly useful as an enabling tool for biocompatible micromachines for medicine transportation and medical examination and treatment, for which an appropriate machine driving mechanism is highly desired. Ormos et al. [9] drove a 5-μm-diameter rotator by laser tweezers and attained a rate of rotation that was linearly proportional to the laser intensity, 2 s⁻¹ for 20 mW; one of the current authors [3] launched the oscillation of a 300-nm-diameter spring and measured a spring constant 3 orders smaller than that extrapolated according to the structural and material parameters of the spring; Maruo et al. [10] trapped a portion of a microneedle to perform several types of motions, like rotation and translation. All microstructures mentioned here were created by the two-photon-induced polymerization of resins and were driven by laser tweezers. These works are critical for exploring the microdevice behaviors to understand nanomechanics of machine motion. However, the utility of the optical driving mechanism is limited, and it is difficult, for example, to operate a micromachine placed inside a blood vessel by this means. In this Letter, we solve the problem by doping surface-modified Fe₃O₄ nanoparticles into resins, from which magnetically active micronanomachines are produced by pinpoint laser writing, and remote control of the machines is realized with a simple ferromagnet.

Figure 1 illustrates the experimental scheme of cosedimentation [11–13]. To synthesize the Fe₃O₄ particles, FeCl₃·6H₂O (5.38 g) and FeCl₂·4H₂O (1.98 g) was dissolved by deionized water (200 ml) under N₂ gas protection. Ammonia aqueous solution (25%, 7 ml) was quickly charged into the solution with vigorous stirring, and the solution was stirred for an additional 3 h at room temperature. The resultant black powder, collected by a ferromagnet and washed three times with deionized water, is desired ferric oxide particle cores. To further dope the powder into a photopolymerizable resin, the surface of the particles has to be chemically modified (Fig. 1). For this purpose, the powder was mixed with deionized water (200 ml) in a flask, into which surfactant oleic acid (OA, 1.22 g) was drop-wise added. The mixture was stirred for 30 min at 80°C under N₂ gas protection and then was washed three times with hexane, giving rise to OA–ferric oxide particles.

Fundamental properties of the synthesized sample were studied. Shown in Fig. 2(a) is the transmission electron microscopic (TEM) image of the OA–ferric oxide particles, showing an average particle size, although not homogeneous, around 10 nm. X-ray dif-
fraction (XRD) curves [Fig. 2(b)] exhibit strong reflection peaks in the 2θ region of 20°–70° in samples both before and after the surface modification. The identical peaks could be assigned to originate from reflections by (220), (311), (400), (422), (511), and (440) planes of Fe₃O₄ crystals, matching well with its standard cubic inverse spinel structure [14]. These results confirm that the particles are indeed of nanosize as expected, and they are in the crystalline status of Fe₃O₄. In other words, OA–Fe₃O₄ nanoparticles have been obtained through the above technical sequence.

An important issue of concern is the magnetic property of the synthesized OA–Fe₃O₄ nanoparticles. From the hysteresis loop acquired from vibrating sample ferromagnetometry (Fig. 3), remanence (0.26 emu/g), and coercivity (3.5 Oe, both not shown) were negligible, showing the superparamagnetism of the particles [11]. This is observably different from characteristics of bulk Fe₃O₄, which are ferromagnetic. The particle size-dependent superparamagnetic behaviors are already known [12,13] and can be interpreted by the concept of relaxation of ferromagnetization orientation of particles. The relaxation time from a certain orientation is described by \( \tau = \tau_0 e^{KV/kT} \) [12], where \( K \) is the particle’s anisotropy constant, \( V \) is the particle volume, \( k \) is the Boltzmann’s constant, and \( T \) is the temperature. For a Fe₃O₄ particle with a diameter less than 20 nm, \( KV \) becomes comparable to the thermal energy \( kT \) at 298 K, and the magnetization starts to fluctuate from one direction to another. As a result, the overall ferromagnetic moment of the particle is randomized to zero in a shorter period of time than the experimental time scales at room temperature, and the particle becomes superparamagnetic. The saturation magnetization of the nanoparticles is 48 emu/g (Fig. 3), large enough to assure that they undergo magnetic force under an external ferromagnetic field with gradient after being magnetized. Experimentally a commercially available cylindrical ferromagnet (the right inset of Fig. 3) with a surface field strength of ~2000 Oe was utilized to manipulate the particles and the microdevices. Here the 10 nm particle size is critical. On one hand it provides sufficient magnetism to sense the external field changes, and on the other hand the size is not too large to affect the surface quality of fabricated devices [15].

To magnetically realize active micronanomachines, the OA–Fe₃O₄ magnetic nanocrystals were further dispersed into photopolymerizable resins. The initial photosresist we used consisted of 37.14 wt. % methyl acrylate as monomer, 60.00 wt. % pentaerythritol triacrylate as crosslinker, 1.66 wt. % benzyl as photoinitiator, and 1.20 wt. % 2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl) butan-1-one as photosensitizer. After doping with OA–Fe₃O₄ nanoparticles (Fig. 1), homogeneously dispersed solution becomes visible, for which the use of OA for preventing nanoparticles from aggregation is essential. The concentration of Fe₃O₄ in the resin mixture is, according to thermogravimetric analysis measurement, around 2.40 wt. %. The resin was pinpoint written according to computer programs by femtosecond laser pulses from a mode-locked Ti:sapphire laser of 790 nm central wavelength, 120 fs pulse duration, and 80 MHz repetition rate. The laser beam was tightly focused by a 100× oil immersion objective lens with a high NA of 1.35, and the focal spot was scanned laterally by steering a two-galvano-mirror set, and the same focal spot was scanned along the optical axis by a piezo stage. After fabrication, the entire structure was rinsed with acetone for 5 min as removed unpolymerized resin, leaving a solidified machine structure. Because of the linear absorption of the black Fe₃O₄, photons are feasible to be directly captured by nanoparticles instead by photoinitiator molecules. This significantly affects the threshold of two-photon photopolymerization of the resin [16,17] and experimen-
tally an average 2 times increase was measured. As a result, 10–12 mW laser power measured before the objective lens, a 50 nm scanning step length, and a 1 ms exposure duration of each voxel were adopted. The achievable height of structures, determined by the working distance of the objective lens, is around 200 μm. Moreover, the resolution of fabrication was observed significantly degraded because of the scattering by nanoparticles of tens of nanometer diameters and because of the reduction of the viscosity of the doped photopolymer. The surface roughness and the smallest diameter of suspended lines are around 40–50 nm (8μm × 8 μm area, the inset of Fig. 3) and 600 nm, against 10 nm [15] and 300 nm [3] for those achieved with undoped photopolymers, respectively.

Shown in Fig. 4(a) is a microspring, with one end fixed to a polymerized anchor that was attached to a glass substrate, and the other end polymerized into a sphere shape. Since the structure contains Fe₃O₄ nanoparticles, it should respond to the stimuli of the exerted magnetic field if a field gradient exists. A paramagnetic object tends to move in the direction of magnetic field strength increases. Thus, by shifting the position of the ferromagnet at the side of the microspring, various motions have been induced; for example, it was elongated [Fig. 4(b)] from the natural state [Fig. 4(a)] and bent to the right side [Fig. 4(c)] and to the left side [Fig. 4(d)]. Here the spring was immersed into acetone and placed under an optical microscope. The spring motion was observed sensitively following the movement of the ferromagnet. When the ferromagnet was withdrawn far, the spring was recovered to its initial situation owing to the superparamagnetic nature of the nanoparticles; as long as the external ferromagnetic field disappeared, the overall moment of the particle is randomized to zero. In pH standard buffer solution and in organic solvents, the spring was similarly manipulated by the external ferromagnet, and the elasticity of the microspring did not seem to be affected.

In conclusion, we demonstrated a scheme of a remotely controllable microspring as an example of micromachines produced by two-photon polymerization of surface-modified Fe₃O₄ nanoparticle-doped resin. The structure motion was found sensitive to the strength change of an external magnetic field. The concept can be extended to more functional micromachines and will thereby open a huge potential for design of new material combinations with novel devices for nano and biological researches.

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References

Fig. 4. (Color online) Photographs of a magnetically remote-driven microspring: (a) the microspring at its natural state, (b) elongated, (c) right bent, and (d) left bent.