Research Article

A Laser Fabrication of Magnetic Micromachines by Using Optimized Photosensitive Ferrofluids

Ye Tian and Xiangxin Shao

College of Electrical and Electronic Engineering, Changchun University of Technology, Changchun 130012, China

Correspondence should be addressed to Xiangxin Shao; shaoliangxin@163.com

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We report here a laser fabrication of magnetic micromachines by using optimized photosensitive ferrofluids. Fe_3O_4 nanoparticles were prepared by thermal decomposition and subsequent ligand exchange. And then, they were dispersed into photoresist. As a representative illustration, a magnetic microturbine with high surface flatness was fabricated, and its rotation speed could reach as high as 400 rpm under revolving magnetic field.

1. Introduction

Laser micronanofabrication technology through two-photon photopolymerization (TPP) of resins has emerged as an interesting tool for the fabrication of micromachines due to their reasonably high spatial resolution and three-dimensional (3D) processing capability [1–5]. To date, various micro-nanodevices such as moveable needle pairs [6], micro-oscillators [7], microspring [8], and microrotators [9] have been successfully fabricated through the laser processing. However, it is very difficult to manipulate these tiny devices in a controlled manner. At present, a vast majority of them are manipulated by optical driving manner which needs a sharply focused laser [6, 10]. The half-contact of this mechanism limits the applications of micromachines in some special fields, for example, operating a micromachine in blood vessel for thrombolytic therapy. Therefore, an appropriate driving mechanism is highly desired [11–14]. Here we solved the problem by doping surface modified Fe_3O_4 nanoparticles in photopolymerizable resins, from which magnetic micromachines are produced by TPP. Then, remote control of these micromachines is readily realized by external magnetic field. Finally, as an example of a promising application, a microturbine was fabricated in the intersection of a “Y” shape microfluidic channel. It would work as an active mixer in magnetic field.

2. Experimental

Monodisperse Fe_3O_4 nanoparticles were synthesized using thermal decomposition method [15]. 2 mmol $\text{Fe}(\text{acac})_3$, 10 mmol 1,2-hexadecanediol, 6 mmol oleic acid, 6 mmol oleylamine, and 20 mL phenyl ether were mixed and magnetically stirred under a blanket of nitrogen. The mixture was heated to 200°C and stayed for 30 min and heated to reflux (300°C) for 2 h. And then it was cooled to room temperature. When 40 mL ethanol was added to the mixture, a black material was precipitated and separated by centrifugation (7000 rpm, 10 min). The black product was then dissolved in 20 mL hexane. Centrifugation (9000 rpm, 10 min) was applied to remove any undispersed residue. The product, 6 nm Fe_3O_4 nanoparticles, was then precipitated with ethanol, centrifuged (7000 rpm, 10 min) to remove the solvent, and redispersed into butyl methacrylate.

For improving their compatibility in photoresists, surface modification process was performed. Typically, 100 mg of oleic acid stabilized Fe_3O_4 nanoparticles was dispersed in 20 mL of propoxylated trimethylolpropane triacrylate ($\text{PO}_3\text{-TMPTA}$, a kind of cross-linker) and stirred for 24 h at room temperature. After that the nanoparticles were dispersed homogeneously in $\text{PO}_3\text{-TMPTA}$. Subsequently, the nanoparticles were washed with ethanol for three times with the help of a magnet. The nanoparticles were kept

FIGURE 1: TEM images of different Fe₃O₄ nanoparticles. (a) Oleic acid stabilized Fe₃O₄ nanoparticles prepared using thermal decomposition method. (b) PO₃-TMPTA modified Fe₃O₄ nanoparticles. The scales in images are 20 nm. (c) TGA curve of the photosensitive ferrofluid.

in butyl methacrylate under the protection of N₂. After ligand exchange process, PO₃-TMPTA was modified on the surface of nanoparticles, and then the nanoparticles could be homogeneously dispersed into acrylate-based photopolymerizable resin consisting of butyl methacrylate (36 wt.%) as monomer, PO₃-TMPTA (56 wt.%) as cross-linker, and 2,4,6-trimethylbenzoyldiphenylphosphine oxide (4 wt.%) and phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (4 wt.%) as photoinitiators.

Using this ferrofluid photoresist, microturbines were fabricated by pinpoint laser writing. In this work, femtosecond laser pulses were tightly focused into the resin by a 60x oil immersion objective lens with a high numerical aperture (NA = 1.35). The central wavelength of the laser was 790 nm with a pulse width of 120 fs and a repetition rate of 80 MHz. The laser focal spot point was scanned point by point in the lateral dimensions by a galvano mirror pair and in the lengthwise dimension by a piezo stage. The scanning step length was 100 nm. The polymerization was induced under the condition of 6.5 mW laser power before the objective lens and of 500 ms exposure duration at each dot. The complete process of fabrication was controlled exactly by computer. Finally, the whole structures were immersed in ethanol for 1 min to remove the unpolymerized resin, leaving a solidified skeleton.

3. Results and Discussion

In order to evaluate the particle size and uniformity, both as-synthesized and modified Fe₃O₄ nanoparticles are characterized by TEM (Figures 1(a) and 1(b)). Statistical results show that nanoparticles before and after modification are well monodispersed and homogeneous. The average diameter of as-synthesized nanoparticles is about 6 nm. After surface modification, a slight increase to ~8 nm is observed. Thermogravimetric analysis (TGA) measurement gives the direct evidence of surface modification. Figure 1(c) is TGA curve of the photosensitive ferrofluid. There is a two-step mass loss in the TGA curve. The first mass loss of 82 wt.% from 200°C to 450°C is due to the thermal decomposition of photoresist, and the second mass loss of 13.5 wt.% from 450°C to 570°C is attributed to the thermal decomposition of chemisorbed 6-(methacryloyloxy) hexanoic acid on particles surfaces. The remaining mass of 4.5 wt.% is attributed to Fe₃O₄ in the resin.

The concentration of Fe₃O₄ nanoparticles in the resin mixture is crucial. The turbine could not correspond to the rotating external magnetic field when the concentration is too low. However, when the nanoparticles concentration is too high, the scattering and linear absorption of nanoparticles will highly increase, which would lead to more roughness of

FIGURE 2: Remote control of microturbine. (a) SEM image of Fe_3O_4 nanoparticle-contained microturbine. (b)–(f) Optical microscopy images of the microturbine in a circumgyratetion cycle. The positions of the point on the turbine blade were marked in the images.

the microdevices. In the experiments, the concentration of Fe_3O_4 in the resin mixture is kept from 4 wt.% to 5 wt.%.

As a representative illustration, microturbines are created by TPP of the ferrofluid photoresist (Figure 2(a)). Because the modification of nanoparticles enhances the compatibility between nanoparticles and photoresist, the surface of microturbines is much smoother. As a result, when the microturbines rotate, the surface friction of them decreases significantly, and the stability and efficiency of microturbines are improved evidently. Figures 2(b)–2(f) are optical microscopy images of the microturbine in a circumgyratetion cycle. For remote control of the microturbine, a piece of ferromagnet is placed on a vortical device around the objective lens which could provide about 4000 gauss magnetic field. For observation of the microturbine working, a point was

fabricated on the turbine blade. Due to the fast speed of rotation, the images of the point become a little fuzzy. The maximum rotating speed of the microturbines containing modified Fe_3O_4 nanoparticles is as high as 400 r/min.

The fabrication of such magnetic microdevices is not limited to flat substrates. As shown in Figure 3, a magnetic microturbine is successfully prepared in the intersection of a “Y-” shape microfluidic channel. It is well known that mixing is very difficult in microscale. Such a complex three-dimensional structure could be regarded as a passive mixer in the channel. When it rotates in magnetic field, the turbine could be regarded as an active mixer. As an effectively mixing device, it could be used to solve the problem of solvents mixing in microscale.

FIGURE 3: Microturbine fabricated with magnetic photoresist containing PO_3 -TMPTA modified Fe_3O_4 nanoparticles in the “Y” shape channel of a microchip.

4. Conclusions

In summary, we have successfully prepared a photosensitive ferrofluid by homogeneously doping the surface modified Fe_3O_4 nanoparticles into acrylate-based photopolymers. The ferrofluid photoresist was utilized to fabricate high quality microturbines for remote manipulation under external magnetic field.

Competing Interests

The authors declare that they have no competing interests.

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