

High performance magnetically controllable microturbines†‡

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Reported in this paper is two-photon photopolymerization (TPP) fabrication of magnetic microturbines with high surface smoothness towards microfluids mixing. As the key component of the magnetic photoresist, Fe₃O₄ nanoparticles were carefully screened for homogeneous doping. In this work, oleic acid stabilized Fe₃O₄ nanoparticles synthesized *via* high-temperature induced organic phase decomposition of an iron precursor show evident advantages in particle morphology. After modification with propoxylated trimethylolpropane triacrylate (PO₃-TMPTA, a kind of cross-linker), the magnetic nanoparticles were homogeneously doped in acrylate-based photoresist for TPP fabrication of microstructures. Finally, a magnetic microturbine was successfully fabricated as an active mixing device for remote control of microfluids blending. The development of high quality magnetic photoresists would lead to high performance magnetically controllable microdevices for lab-on-a-chip (LOC) applications.

Introduction

Recently, enormous progress has been made in microfluidic chips due to their distinct advantages compared with a macroscopic reaction setting.^{1–3} Typically, microfluidic chips allow chemical or biological reactions to occur in a safe, low-consumption, environment-friendly and efficient manner, which is of benefit to convenient handling of reactions from reactants mixing to products separation. However, unlike in a macroscopic reactor, microfluidic flow in a microchannel is usually difficult to control, because laminar flow is dominant in this case. For example, considerable difficulties arise when two or more kinds of microfluids need to be mixed homogeneously in microchannels under low Reynolds number condition. However, effective mixing, which could significantly reduce reaction time and enhance reaction yield, is essential for most microfluidic reactions. Therefore, considerable efforts have been devoted to develop mixing techniques for lab-on-a-chip (LOC) applications.^{4–8} Typically, passive mixing devices, such as zigzag channels,⁹ split-and-recombine channels,¹⁰ modified Tesla structure,¹¹ and active mixing devices based on acoustic streaming,¹² ultrasound,¹³ piezoelectric vibrating,¹⁴ low frequency vibration¹⁵ and electrohydrodynamic technique,^{16–19} are successfully developed for microfluids mixing. Nevertheless, the passive mixing manner suffers from poor capability for localized blending and precise temporal control, and the active mixing routes usually require an external power source and

wireleads which make the microchannel package very complex.^{20,21} Therefore, it is extremely desirable to develop telecontrolled microdevices for localized microfluids mixing.

A magnetic microstir-bar was successfully created for microfluids mixing.²¹ However, the micromotors and microchannels were fabricated synchronously through lithographic routes, thus the method is incompatible for integration with existing microchannels which are uneven. Two-photon-photopolymerization^{22–24} has been proven to be a powerful technique for fabrication and functionalization of microfluidic chips.²⁵ Recently, we have reported a novel remote manipulation of magnetic micro-nanomachines which were prepared by two-photon photopolymerization of Fe₃O₄ nanoparticle doped photoresist.²⁶ This magnetic driving technique contributes great potential for LOC applications.²⁷ However, the precise microfluidic chips make higher requirements on the quality of the telecontrolled microdevices. For example, surface friction plays a dominant role in the performance of the moving micromotors,^{28,29} and therefore, a smooth surface is essential for micromachines used for LOC.

In this paper, we developed a new magnetic photoresist for TPP fabrication of microturbines with much smoother surfaces. As compared with commonly used Fe₃O₄ nanoparticles prepared by coprecipitation of Fe²⁺ and Fe³⁺ ions in the presence of ammonia,³⁰ magnetic nanoparticles synthesized *via* high-temperature induced organic phase decomposition of an iron precursor³¹ show much smaller particle size and uniform particle shape, which impart morphological advantage for doping in photoresist. Through a post surface modification for compatibility improvements,^{32,33} the magnetic nanoparticles were homogeneously dispersed in acrylate-based polymeric monomers, forming a transparent magnetic photoresist. As a representative example, magnetic microturbine with improved surface roughness was successfully fabricated, which can be remotely manipulated towards microfluids mixing. The novel TPP fabrication of high performance magnetic microdevices shows great potential for microfluidic chip functionalization.

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Experimental

Preparation of magnetic nanoparticles

Oleic acid stabilized Fe_3O_4 nanoparticles were synthesized by thermal decomposition of an iron precursor according to the literature.³¹ For improving their compatibility in photoresists, surface modification process was performed. Typically, 100 mg of oleic acid-stabilized Fe_3O_4 nanoparticles were dispersed in 20 ml of propoxylated trimethylolpropane triacrylate ($\text{PO}_3\text{-TMPTA}$), and stirred for 24 h at room temperature. After that the nanoparticles were dispersed homogeneously in $\text{PO}_3\text{-TMPTA}$, and a transparent dark brown solution was obtained. Subsequently, the nanoparticles were washed with ethanol for three times with the help of a magnet. The nanoparticles were kept in butyl methacrylate under the protection of N_2 .

For comparison, Fe_3O_4 nanoparticles were also prepared by coprecipitation of Fe^{2+} and Fe^{3+} ions in the presence of ammonia according to the literature.³⁰

Preparation of magnetic photoresists

Magnetic photoresists were achieved by dispersing the Fe_3O_4 nanoparticles (~ 5 wt. %) into the conventional photoresist which consists of butyl methacrylate (36 wt.%) as monomer, $\text{PO}_3\text{-TMPTA}$ (56 wt.%) as crosslinker, 2,4,6-trimethylbenzoyldiphenylphosphinoxid (4 wt.%) and phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (4 wt. %) as photoinitiators. The homogeneous mixture was obtained with the help of ultrasonic vibration.

Fabrication of micro-structures

For fabrication of microcubes, femtosecond laser pulses were tightly focused into the resin by a $100\times$ oil immersion objective lens with a high numerical aperture ($\text{NA} = 1.40$). 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 50 nm. The polymerization was induced under the condition of 11 mW laser power before the objective lens and of 100 μs 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, and then kept in ethanol.

For fabrication of microturbines, a $60\times$ oil immersion objective lens was used to focus laser pulses into the resin, and its numerical aperture was 1.35. The scanning step length of the laser focal spot point was 100 nm. The laser power was 6.5 mW and the exposure duration was 500 μs .

Results and discussion

Surface modification of Fe_3O_4 nanoparticles

Dispersibility of the magnetic nanoparticles is crucial to preparation of magnetic photoresists. In order to obtain a improved compatibility in general photoresists such as acrylate species, surface modification is essential. In our experiments, Fe_3O_4 nanoparticles were synthesized *via* thermal decomposition

method.³¹ The as-synthesized nanoparticles were stabilized with oleic acid, which significantly debased their dispersibility in acrylate-based photoresist due to their different polarity. As shown in Fig. 1a, the oleic acid-stabilized nanoparticles can be dispersed homogeneously in nonpolar solvent of *n*-hexane (*n*-HA), while they precipitate immediately in polar solvents such as methyl acrylate (MA), ethanol and THF. Under magnetic field, the nanoparticles could be separated from the solvent of MA. Herein, $\text{PO}_3\text{-TMPTA}$ was used as surface modificative agents to improve their compatibility in MA. After modification, the nanoparticles can be no longer dispersed in *n*-hexane, whereas they can be well dispersed in MA. This distinct change of dispersibility indicates the successful modification of $\text{PO}_3\text{-TMPTA}$ on the surface of the nanoparticles. The solution is so stable that it can be kept in MA for more than a month. Even under gravitation, these magnetic nanoparticles are still dispersed homogeneously without separation from the solvent.

Magnetic hysteresis loops show that both nanoparticles before and after surface modification are superparamagnetic (Fig. 1b). The saturation magnetizations of the oleic acid-stabilized and $\text{PO}_3\text{-TMPTA}$ modified nanoparticles are 56 and 54 emu/g, respectively. The change of the saturation magnetization is attributed to the slight weight increase after surface modification. Thermogravimetric analysis (TGA) measurement confirms this weight change. As shown in Fig. 1c, $\text{PO}_3\text{-TMPTA}$ modified sample shows a larger weight loss than oleic acid-stabilized sample. The two curves exhibit different weight loss in the temperature range from 300 to 800 $^\circ\text{C}$, which were attributed to the decomposition of oleic acid and $\text{PO}_3\text{-TMPTA}$ layer, respectively.

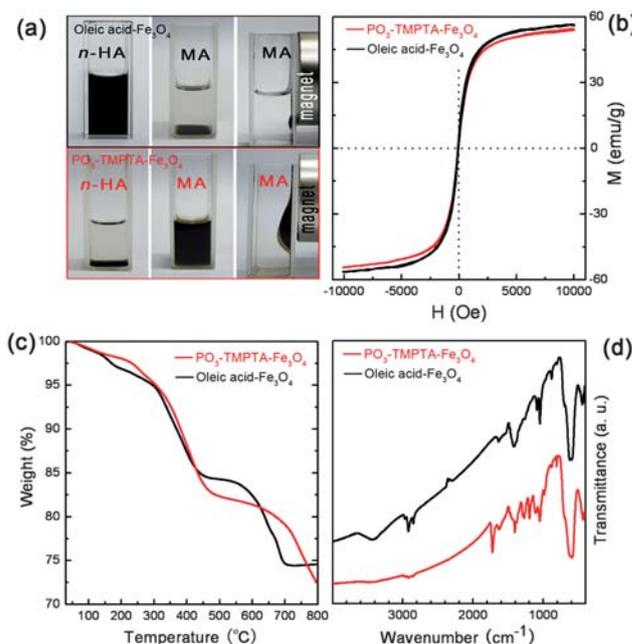


Fig. 1 (a) Photographs of oleic acid coated and $\text{PO}_3\text{-TMPTA}$ modified Fe_3O_4 nanoparticles dispersed in the solvents of *n*-hexane (*n*-HA) and methyl acrylate (MA); (b) VSM curves, (c) TG curves and (d) FT-IR spectra of oleic acid coated and $\text{PO}_3\text{-TMPTA}$ modified Fe_3O_4 nanoparticles.

FT-IR spectra of oleic acid-coated and PO₃-TMPTA modified Fe₃O₄ nanoparticles give direct evidence of the successful modification of PO₃-TMPTA molecule. As shown in Fig. 1d, the strong peaks at 2921, 2850 and 1424 cm⁻¹ are attributed to oleic acid.^{34,35} The characteristic peak of free carboxylic groups (around 1720 cm⁻¹) disappears, suggesting that the carboxylic groups are anchored on the surface of Fe₃O₄ nanoparticles. The FT-IR spectrum of PO₃-TMPTA stabilized nanoparticles shows typical peaks of C=O (1724 cm⁻¹) and C-O (1194 cm⁻¹), which are related to the presence of PO₃-TMPTA. The peaks around 605 cm⁻¹ are assigned to Fe₃O₄ nanoparticles.

Fe₃O₄ nanoparticles comparison

Fig. 2 shows the TEM images of Fe₃O₄ nanoparticles prepared by coprecipitation and thermal-decomposition. As shown in Fig. 2a, coprecipitation-synthesized Fe₃O₄ nanoparticles agglomerate seriously. Statistic data shows that the particles have broad size distribution (5–22 nm). As a comparison, Fe₃O₄ nanoparticles synthesized *via* thermal-decomposition are monodisperse and have uniform shape. The particle size distribution is very narrow and the average size is about 6 nm (Fig. 2b). It is worthy of pointing out that the as-synthesized Fe₃O₄ nanoparticles are stabilized with oleic acid, and thus a self-assembly phenomenon can be observed from the TEM image. After surface modification, as shown in Fig. 2c, the particle is still

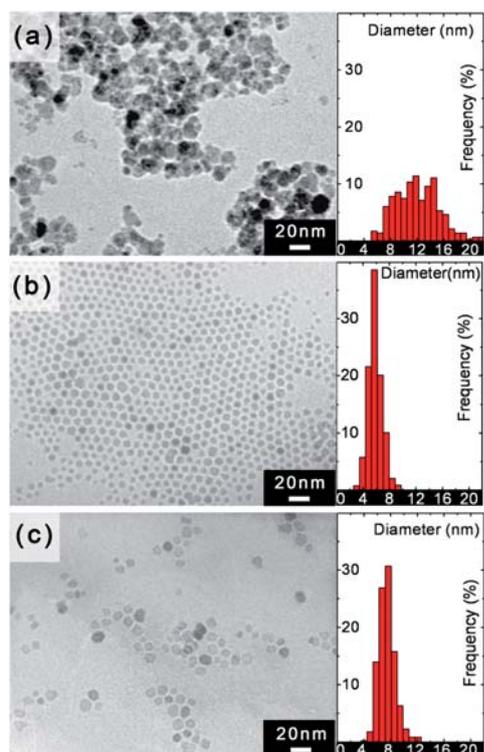


Fig. 2 TEM images and particle size distributions of different Fe₃O₄ nanoparticles. (a) Fe₃O₄ nanoparticles synthesized *via* coprecipitation method, (b) oleic acid stabilized Fe₃O₄ nanoparticles prepared using thermal-decomposition method, (c) PO₃-TMPTA modified Fe₃O₄ nanoparticles. The right figures are the particle size distributions. Statistic results were obtained by measuring 1000 nanoparticles.

uniform and the statistic data reveals a slight increase of average particle size to about 8 nm due to the PO₃-TMPTA layer on the particles surface.³⁶

Fabricative quality comparison

In order to screen a suitable magnetic source for photoresist doping, the fabricative quality of the two kinds of photoresist doped with different Fe₃O₄ nanoparticles is also evaluated. As an example, two micro-cubes were fabricated for the measurement of surface roughness. Fig. S1 (ESI† and inset of Fig. 3) shows the SEM images of these two microcubes. Obviously, the cube with coprecipitation-synthesized nanoparticles has a much rougher surface than the one with thermal-decomposition synthesized nanoparticles. AFM images (Fig. 3) give direct evidence of surface roughness. As shown in Fig. 3a, the surface of the microcube containing coprecipitation-synthesized Fe₃O₄ has agglomerated nanoparticle clusters. For the surface of micro-machines, this kind of roughness would significantly influence their performance. On the contrary, the surface of a microcube containing PO₃-TMPTA modified Fe₃O₄ nanoparticles is much smoother (Fig. 3b). Height proof and 3D transformed AFM images of these two surfaces give clear comparison. As a conclusion, the photoresist with PO₃-TMPTA modified Fe₃O₄ nanoparticles which is prepared by thermal-decomposition route is more suitable for fabrication of functional micromachines.

Fabrication and remote control of microturbine

The influence of surface roughness would be enlarged in complex microstructures. In this work, we fabricated microturbines as active mixing devices for LOC applications. Fig. 4 shows the comparable SEM images of microturbines. The microturbine containing coprecipitation-synthesized Fe₃O₄ nanoparticles is about 28 μm in diameter (Fig. 4a), and has a slight distortion. Remote control of the microturbine is performed by immersing it in acetone with an extra rotating magnetic field (for details

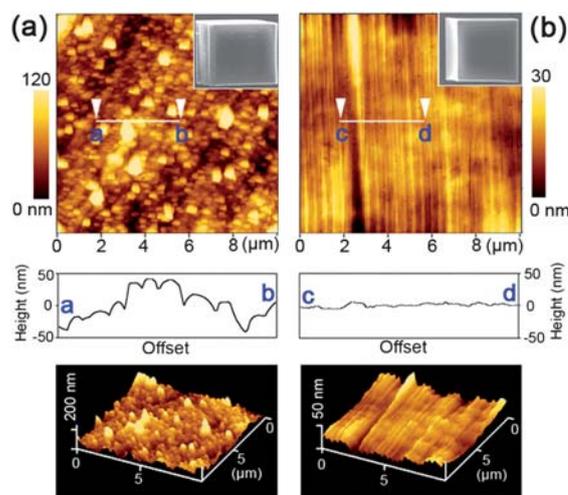


Fig. 3 AFM images, height profile and 3D transformed images of microcube surfaces fabricated with magnetic photoresist containing (a) coprecipitation-synthesized Fe₃O₄ nanoparticles and (b) PO₃-TMPTA modified Fe₃O₄ nanoparticles. Insets are SEM images of microcubes.

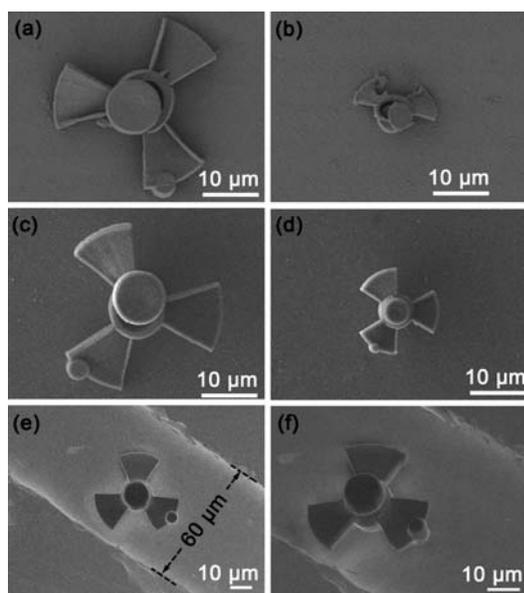


Fig. 4 SEM images of microturbines fabricated with magnetic photoresist containing (a, b) coprecipitation-synthesized Fe_3O_4 nanoparticles and (c, d) magnetic photoresist containing PO_3 -TMPTA modified Fe_3O_4 nanoparticles; (e, f) microturbine fabricated with magnetic photoresist containing PO_3 -TMPTA modified Fe_3O_4 nanoparticles in the channel of a microchip.

see ESI†). As shown in the supporting video (ESI,†Video S1), the stick-slip phenomenon is dominant in the motion of this microturbine. When the fabricative size of the turbine decreases, higher fabricating precision is required. In this condition, the photoresist with coprecipitation-synthesized nanoparticles can not be made a complete microstructure (Fig. 4b). On the contrary, the microturbine fabricated with the photoresist which is doped with PO_3 -TMPTA modified Fe_3O_4 nanoparticles is perfect even when the scale is reduced to about $14\ \mu\text{m}$ in diameter. The rotating video shows that the performance of this microturbine is very stable, and the motion is very agile. The rotating rate is measured to be about 300 rpm in acetone (ESI,†Video S2). The fabrication of this mixing microdevice is not limited to flat substrates, as exhibited in Fig. 4e and f, microturbines could also be fabricated in a microfluidic channel. By using a rotating magnetic field, the microturbine could be remotely manipulated for efficient mixing.

Conclusions

In summary, a novel magnetic photoresist which consists of acrylate-based polymeric monomer and magnetic nanoparticles was successfully developed for fabrication of microturbines towards remote control of microfluids mixing. After careful comparison, PO_3 -TMPTA coated Fe_3O_4 nanoparticles prepared by thermal decomposition of iron precursor and subsequent surface modification were considered as a suitable magnetic doping agent for photoresist towards high quality micro-fabrication. Typically, a magnetic microturbine was successfully

fabricated and the rotating motion could be realized by using an extra rotating magnetic field. As an active mixing device, this novel microturbine shows great potential for LOC applications.

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