

CHEMICALLY ROBUST, RAPIDLY PRINTED POLYURETHANE MICROREACTOR FOR SYNTHESIS OF MONODISPERSE MAGNETIC IRON OXIDE NANOPARTICLES

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ABSTRACT

This paper introduces a novel fabless, polyurethane microfluidic reactor (PMR) for the production of magnetic nanoparticles using droplet-based flow. The PMR system is the most chemically robust polymer platform to date for nanoparticle synthesis; unlike other polymeric microfluidic platforms such as polydimethylsiloxane (PDMS), it does not absorb aqueous solvents, alcohols or organic materials [1]. This provides the unique capability to rapidly design and fabricate the reactor for various chemistries at low cost. We have synthesized iron oxide nanoparticles as a test case due to their broad applications in biological labeling.

KEYWORDS: Microreactor, Polyurethane, Droplet Microfluidics, Iron Oxide Nanoparticles, Magnetic Nanoparticles, CO₂-laser

INTRODUCTION

Microreactors have several advantages over conventional batch-wise methods for nanoparticle synthesis, such as controllability of reaction conditions, rapid change of reaction parameters and ability to precisely control reagent concentrations [2]. This precise level of control is needed to synthesize monodisperse nanoparticles with controlled size and shape; therefore microreactors are becoming more popular for the production of nanoparticles.

This paper describes a droplet-based microreactor used for magnetic iron oxide nanoparticle synthesis. Microfluidic channels were fabricated out of a chemically resistant polyurethane (PU) material by using a CO₂-laser and they were bonded to another PU substrate by solvent treatment to create closed channels. Synthesized iron oxide nanoparticles were characterized by transmission electron microscopy (TEM) and x-ray diffraction (XRD). These nanoparticles had diameters of $3\text{nm} \pm 1\text{nm}$ and they were observed to be magnetic.

DESIGN

The microreactor is designed to synthesize iron oxide nanoparticles by a coprecipitation technique that is based on mixing two reagents. The best way to mix two liquids on a small scale is to use a droplet-based system in which the internal flow inside droplets reduces the time required for mixing dramatically [3,4]. Two reagents are introduced into the system and they break-up into droplets inside a carrier fluid at a T junction due to shear forces, as shown in Figure 1. To increase the mixing rate of droplets a channel with a sinusoidal shape is used, which is referred to as the mixing channel. The shape of this channel causes droplets to deform, thereby increasing the internal flow.

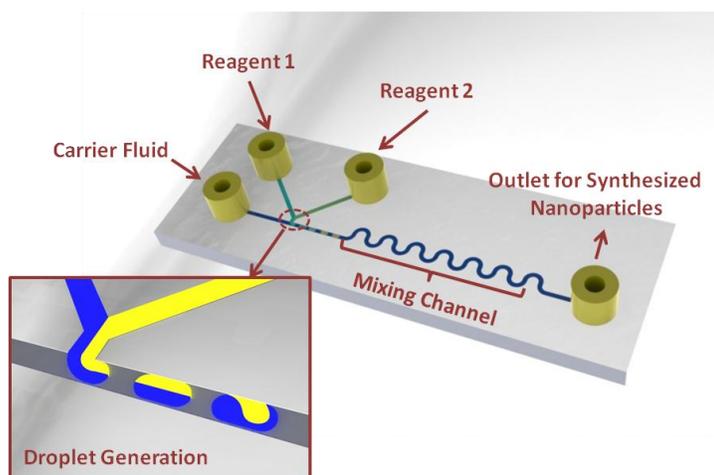


Figure 1: Schematic depiction of the polyurethane substrate microreactor for nanoparticle synthesis.

The synthesis reaction requires specific mixing ratios of reagents determined by the reaction stoichiometry and the concentration of the reagents. In this work the mixing ratio was determined precisely by the flow rates of the reagent streams, controlled by syringe pumps.

FABRICATION

The polyurethane microreactor was directly printed on a cured PU substrate using a CO₂-laser printer (VersaLaser VLS 2.3, Universal Laser Systems) directly from a CAD file, as depicted in Figure 2A. This technique is similar to one previously demonstrated for fabricating poly(methyl methacrylate) (PMMA) microchannels [5]. The fabrication method is very fast; several microreactors can be printed in a few minutes. It is also very inexpensive, since it requires no photo mask. The profile of the microchannel is Gaussian, since it is dependent on the laser intensity distribution [5], and the surface is very smooth (Figures 2B and 2C). The channel width and height both increase with increasing laser power. In this work a laser power of 5.4 W was used. The average width and depth of the channel printed at this power were 375 μm and 110 μm, respectively. A new solvent assisted bonding technique was developed in which dimethylformamide (DMF) was applied on both surfaces to bond cured PU substrates to form closed channels (Figure 2D).

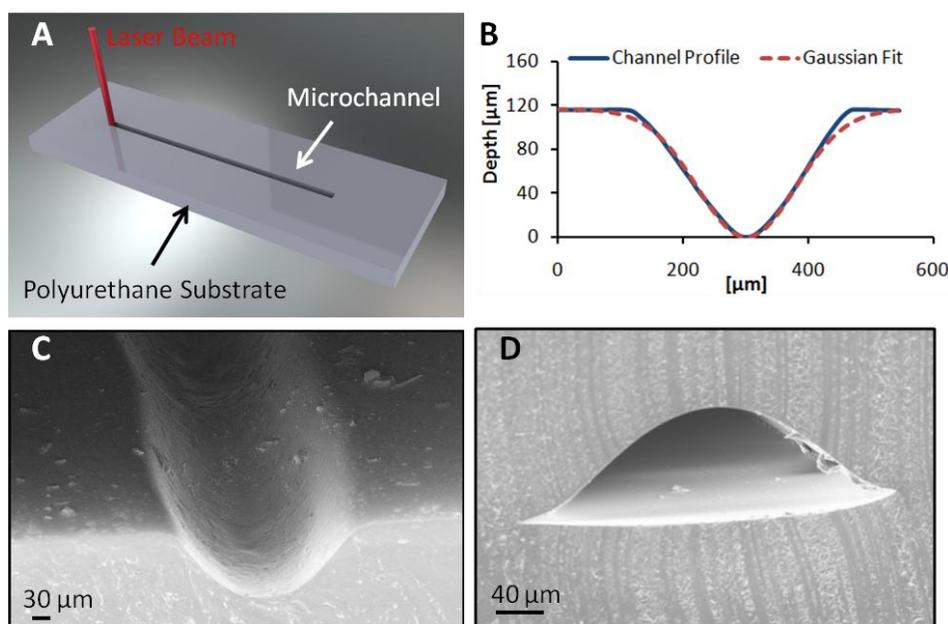


Figure 2: A) Schematic of the laser beam forming the microchannel in the polyurethane substrate. The width and height of the channel is dependent on the laser power. B) Profile of the CO₂-laser engraved channel. Due to the laser intensity distribution, the channel profile is Gaussian. C) SEM image of PU channel formed by CO₂-laser. D) SEM image of the cross section of a channel encapsulated by another PU substrate after DMF treatment.

EXPERIMENTAL RESULTS AND DISCUSSION

Iron oxide nanoparticles were synthesized by hydrolyzing an aqueous mixture containing 0.48 mol/L FeCl₃, 0.24 mol/L FeCl₂ and 0.5 mol/L HCl (reagent 1) using 2M aqueous ammonia (reagent 2) following the method in [4].:



Both solutions were prepared with DI water degassed under argon gas to minimize oxidation of iron (II) during reaction. The reaction was also carried out under argon. The microreactor was not degassed before use because, unlike materials such as PDMS, PU has a very low permeability to gas, and hence would not have retained oxygen.

The two reagents enter the reactor from separate channels, briefly mix and form a droplet in a third channel containing mineral oil as a carrier fluid. Nanoparticles are generated as reaction 1 proceeds inside the droplet. The flow rate of base solution (reagent 2) was twice that of the iron salt solution (reagent 1). When the flow rates were equal, which provided a stoichiometric amount of base, the synthesized particles were non-magnetic. It appears that the higher driving force for reaction 1 provided by supplying excess base was needed to obtain magnetic particles. Real time images of the nanoparticle synthesis inside the microreactor are shown in Figure 3.

The particles were characterized by TEM and X-ray diffraction. Figure 4 shows a TEM image of the synthesized particles. The particles have narrow size distribution compared to batch synthesis techniques. Figure 5 shows the X-ray diffraction pattern. Three of the major peaks appeared to correspond to magnetite, as noted in Figure 5. However, two additional peaks, at 2θ values of about 22° and 48° were not due to magnetite. The first may correspond to goethite, αFeOOH, and the second to the silicon substrate on which the particles were mounted. The precipitate was magnetic; Figure 5B shows the interaction of particles with a magnet in the solution collected directly from the microreactor.

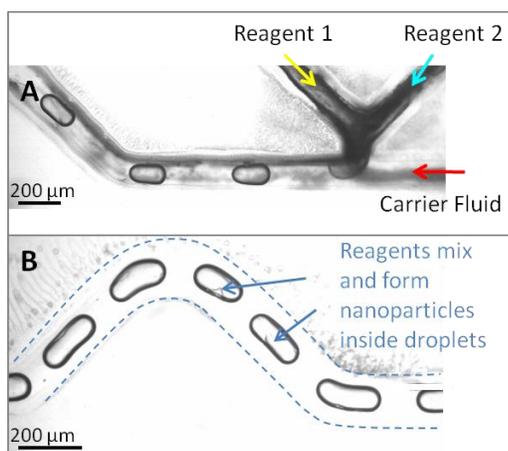


Figure 3: High-speed camera images of the synthesis of nanoparticles inside the microreactor. A) Reagents form a droplet at the T-junction by shear induced break-up. Flow rate of carrier fluid (mineral oil) is 600 $\mu\text{L/hr}$ whereas flow rate of reagent 1 and 2 are 200 $\mu\text{L/hr}$ and 400 $\mu\text{L/hr}$ respectively. B) Reagents are mixed inside droplets while carried by the carrier fluid.

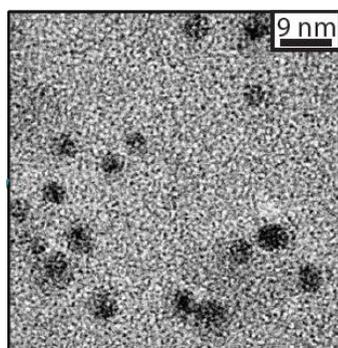


Figure 4: TEM image of iron oxide nanoparticles synthesized inside the microreactor. Particles are 5 ± 0.5 nm in diameter.

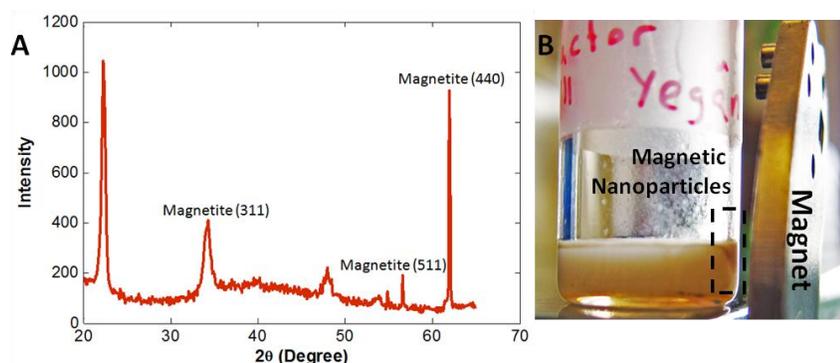


Figure 5: A) X-ray diffraction pattern of nanoparticles synthesized inside the microreactor. The sample is a combination of Fe_3O_4 and $\alpha\text{-FeO(OH)}$. B) Particles are attracted to the magnet when it is brought in close contact. The solution shown here was collected directly from the microreactor before being washed.

CONCLUSION

This paper demonstrates a polyurethane microfluidic reactor that is fabricated by using a CO_2 -laser on a cured polyurethane substrate. Magnetic iron oxide nanoparticles, apparently magnetite, were synthesized in this microreactor; these had a very uniform size distribution. This reactor design could be used to synthesize other types of nanoparticles by using appropriate reagents and controlling the flow rates of reagent streams to obtain the necessary residence times.

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