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Hydrodynamic fabrication and characterization of a pH-responsive microscale spherical actuating element

DuckJoong Kim[a,b], SungRak Kim[a,b], JiYoung Park[a,b,c], JuYeoul Baek[a,b],
SeonJeong Kim[d], Kyung Sun[a,b], TaeSoo Lee[e], SangHoon Lee[a,b,*]

[a] *Department of Biomedical Engineering, College of Medicine, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-701, South Korea*
[b] *Korea Artificial Organ Center, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-701, South Korea*
[c] *Department of Biomedical Engineering, College of Medicine, Dankook University, San 29, Anseo-Dong, Cheonan-city, Chungnam 330-714, South Korea*
[d] *Department of Biomedical Engineering, College of Medicine, Hanyang University, Haengdang-Dong, Seongdong-Gu, Seoul 133-791, South Korea*
[e] *Department of Biomedical Engineering, College of Medicine, Chungbuk University, Gaesin-Dong, Heungdeok-Gu,*
Cheongju-City, Chungbuk 361-763, South Korea

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Abstract

In this paper, we report a hydrodynamic fabrication method for pH-responsive microspheres, which act as an actuating component, and we characterize their volume-changes according to variations in pH values. We fabricated the microsphere-producing apparatus by using a poly(dimethylsiloxane) (PDMS) based substrate and a pulled-glass pipette. The swelling and the shrinking motions that varied according to the size, the shape and the concentration of AA were characterized with alternating application of acidic and basic solutions. The fabricated microspheres exhibited a larger and a faster volume transition than the cylindrical shaped post, which results generally from a conventional in-situ photopolymerization method. The repeated motions resulting from the alternating change of pH value were stable and reproducible. This finding indicates that the produced microspheres can be used as an actuation component in other microdevices. To exemplify such an application, we integrated a single microsphere into a PDMS-based microfluidic valve, and the fabricated microvalve resulted in stable operations relative to pH change.

Keywords: pH-responsive microsphere; Hydrogel; Photopolymerization; Microvalve

1. Introduction

The principal actuating mechanism in living organisms is the conversion of chemical energy into mechanical energy, which amounts to an extremely efficient process. To date, there have been numerous attempts to mimic this actuation method [1–3]. In nature, the most important components of a living cell (proteins, carbohydrates and nucleic acids) are polymers [4], which function broadly as parts of complicated cell machinery. Among man-made products, ionic hydrogels exhibit a volumetric change in response to certain stimuli such as pH, temperature and the concentration of an organic solvent, and these hydrogels' actuating mechanism is very similar to the mechanism underlying living organisms [5,6]. Researchers have made broad use of such stimulus-responsive hydrogels in many fields and have reported on diverse applications, including valves [7], drug-delivery actuators [8], self-regulating devices [9] and artificial muscles [10]. Recently, researchers in diverse fields have applied in-situ photopolymerization to the construction of such hydrogel structures inside microfluidic platforms. This approach has attracted a great deal of attention owing to both the simplicity of the fabrication process and the cost effectiveness of the fabrication process relative to conventional fabrication technology [11,12]. In spite of its many advantages, the in-situ photopolymerization method has many drawbacks. This method requires that researchers have both refined skills and diverse peripheral devices (a UV-exposure device, a syringe pump, etc.) to construct a hydrogel structure inside a microfluidic platform. The microstructure constructed via in-situ photopolymerization is not fully exposed to the pH solution, as both its bottom and its top almost touch the inner surface of the microfluidic channel, and this means that the swelling motion is slow. Furthermore, the mass production of a

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[*] Corresponding author. Tel.: +82 41 550 3893; fax: +82 41 562 7937.
E-mail address: dbiomed@korea.ac.kr (S. Lee).

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microfluidic device containing a responsive hydrogel based on this method is not so easy. The way to overcome these limitations hinges on two factors: the mass production of pH-responsive microspheres outside the channel and the simple integration of a microsphere into the microvalve platform. In this paper, we have presented a method for the mass production of pH-responsive microspheres that act as actuating elements and we have characterized their swelling properties. For the mass production of the microspheres, we used the 'on the fly' photopolymerization method, which our group developed for this very purpose [13,14]. We characterized the microspheres' swelling properties under diverse conditions: (1) microspheres' repeated swelling and shrinking motions as responses to pH-value changes, (2) microspheres' swelling properties as responses to the change of microspheres' size and shape and (3) microspheres' swelling properties as responses to the change of acrylic acid (AA, pH-sensitive monomers) concentration. We integrated the produced microspheres into the PDMS-based valve platform to show the feasibility of the microspheres as actuating components. The suggested fabrication method for microspheres has many advantages such as (1) mass-production capacity, (2) flexibility of size and materials, and (3) cost effectiveness. These microspheres can be broadly employed as actuating components of movable microfluidic devices (e.g. microvalves and micropumps).

2. Fabrication of a pH-responsive microsphere

We prepared a microfluidic apparatus for the fabrication of pH-responsive microspheres, and Fig. 1(a) illustrates the schematics of apparatus. Our group fabricated this apparatus by hybridizing a PDMS substrate and a pulled micropipette, as was reported previously [15]. Into the sample-inlet port, we introduced the polymerizable sample fluid (a mixture of 85 wt% 4-hydroxybutyl acrylate (4-HBA), 11 wt% acrylic acid (AA), 1 wt% ethyleneglycol dimethacrylate (EGDMA) and 3 wt% 2,2-dimethoxy-2-phenyl-acetophenone (DMPA)); and into the sheath-inlet port, we introduced the immiscible non-polymerizable sheath fluid (mineral oil). Droplet formation resulted from the competition between surface tension and shear forces generated at the junction of the two immiscible fluids (the dotted region in Fig. 1(a)). The droplets grew and, after reaching full growth, separated from one another, as Fig. 1(b) illustrates. Floating in the sheath stream, these separated droplets (unpolymerized) moved through the outlet pipette without touching the inner wall. While the droplets were traveling through the outlet pipette, they were exposed to UV light (365 nm, Novacure, Photonic Solutions Inc.). Then the moving droplets polymerized, and the solidified microspheres extruded out the outlet pipette. We can calculate the size of the microspheres under external shear force by equating the Laplace pressure with the shear force:

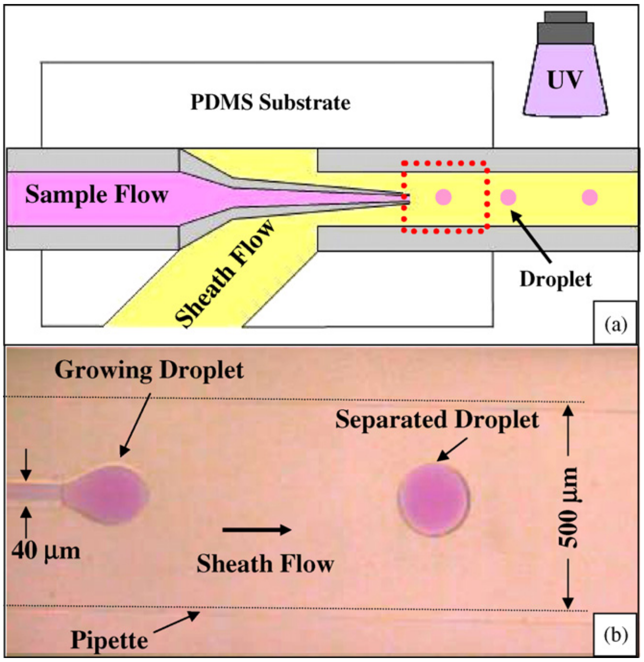

Fig. 1. (a) Schematic diagram of pH-responsive microspheres' production system and (b) the droplets at the tip of the sharp pipette.

$$r \sim \frac{\sigma}{\eta\varepsilon}, \tag{1}$$

where r is the final droplet radius, σ is the interfacial tension between the water/oil, η is the viscosity of the continuous phase and ε is the shear rate [16].

3. Experiments

To examine the volume-transition properties of the pH-responsive microspheres, we fabricated the PDMS-based microfluidic test device, and its schematic diagram is illustrated in Fig. 2. This device consists of three inlet ports, a micro-dam that holds the microsphere inside the channel, and one outlet port. During the fabrication process of the test device, we incorporated two same-sized microspheres at the position represented by the dotted rectangular lines in Fig. 2. The central inlet port supplied water for the rinsing of the channel, and the basic and the acidic solutions were introduced through the other inlets ports. For the injection of fluids, three syringe pumps were employed. By making alternating additions of the basic and the acidic solutions, we measured the degree of swelling and shrinking quantitatively, and we calculated the swelling ratio, which reflects the degree, according to Eq. (2):

$$\text{swelling ratio}\,(\%) = \frac{\text{volume}_t - \text{volume}_{t0}}{\text{volume}_{t0}} \times 100, \tag{2}$$

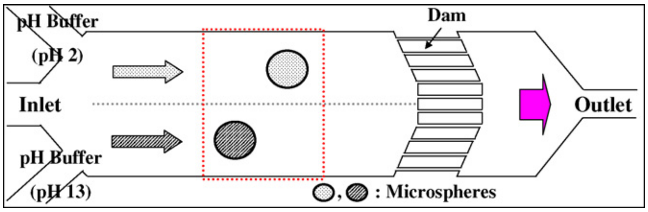

Fig. 2. Schematic of microfluidic device for tests of the swelling and shrinking properties of the pH-responsive microspheres.