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Controlled production of double emulsions in dual-coaxial capillaries device for millimeter-scale hollow polymer spheres

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HIGHLIGHTS

- Designed dual-coaxial capillaries devices for the double-emulsion drops generation.
- Studied the effect of operating conditions on the double-emulsion droplet size.
- Analyzed emulsification in dual-coaxial capillaries from a physical point of view.
- Explained significant effect of inner fluid on droplet generation for each method.
- Fabricated millimeter-sized hollow polymer spheres using the double emulsion drops.

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ABSTRACT

Capillaries-based co-flowing microfluidic devices were designed and then fabricated for the controlled production of water-in-oil-in-water (W/O/W) double-emulsion droplets, where polystyrene dissolved in fluobenzene was employed as the oil phase. Two configurations of the co-flowing devices were employed in the experiments. In the so-called one-step device, the inner capillary tip locates at the same cross-section of the middle capillary tip. Thus, the core drop and the shell drop depart from their capillaries ends simultaneously, forming a double-emulsion drop in one step. While in the so-called two step device, the inner capillary tip locates upstream to the middle capillary tip. The core drop and the shell drop break off from their respective capillaries ends successively, forming a double-emulsion drop in two steps. The effect of the fluids flow rates on the double-emulsion droplets size as well as their formation mechanism was studied comprehensively in the proposed devices. Experimental results implied that slight difference in device configurations would lead to significant difference in droplet formation mechanisms and thus size-control laws. In the two-step device, the inner stream of fluid had little influence on the breakage and the outer diameter of the double-emulsion drops, while in the one-step device the effect was significant. With the produced double-emulsion droplets, millimeter-sized polymer capsules with single hollow cavity and ultra-thin shells were obtained by solidifying the oil layers of the compound drops using the solvent evaporation method.

1. Introduction

Hollow polymer particles with diameters ranging from nanometers to millimeters have wide applications in various fields such as sensors, drug delivery, food industry, pigments, microcapsules and catalyst loading because of their unique properties such as low density, high surface-to-volume ratio and low coefficients of thermal expansion (Cheng et al., 2012; Lou et al., 2008; Sukhorukov et al., 2005; Yamada et al., 2010; Yang et al., 2009). Such particles with different diameters usually lead to different applications. For instance, intravenous injection requires diameters below 1–10 μm; subcutaneous injection requires diameters below 100–120 μm (Benita, 1996; Rosoff, 1989); while many general applications in chemistry require the particle diameters in the order of 100–500 μm (Chiu et al., 2009; Huebner et al., 2008). Besides those micron-scale hollow particles people are quite familiar with in recent years, thin-walled shells with diameters in millimeters have their special applications in the area of high energy density physics, where they are used as cryogenic capsules for laser fusion experiments (Chen et al., 1991; Lambert et al., 1997; Paguio et al., 2006) or mandrels for the fabrication of inertial confinement fusion (ICF) targets (Letts et al., 1995; McQuillan et al., 1997). Among the approaches to producing millimeter-scale polymer shells such as the drop-tower

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methods (Cook, 1995) and the interfacial polymerization techniques (Takagi et al., 1993), the emulsion-based microencapsulation technique (Takagi et al., 1991) is the most straightforward, developed and commonly used one.

Fabrication of hollow polymer spheres using microencapsulation technique consists of three steps: the emulsification of the polymer solution encapsulating other substance(s) and the solidification of the middle layers of the double-emulsion droplets, followed by the removal of the encapsulated substance(s), where the first step determines the final particle size. Since many properties of these hollow particles are size dependent, controlling the particle diameter, shell thickness and their monodispersity is especially important to produce the water–oil–water (W/O/W) double emulsions in practice.

Many researches have been done on the continuous formation of double emulsions with tailored properties using the microfluidic technique based on milli- or micro-channels for the advantages on the precise control over the droplet size as well as their monodispersity (Lao et al., 2009; Lin et al., 2010; Nisisako et al., 2005; Nurumbetov et al., 2012; Okushima et al., 2004; Panizza et al., 2008; Seo et al., 2007). Some microfluidic devices have been developed, e.g., the flow channels fabricated on 2D planar chips and the ones using 3D co-flowing designs (Chu et al., 2007; Kim et al., 2011a, 2011b; Thiele et al., 2010; Utada et al., 2005). Based on the developed milli- or microfluidic devices, numerous experimental or theoretical studies have been conducted on the single-emulsion droplet size (Guillot et al., 2007; Umbanhowar et al., 2000; Utada et al., 2007) and double-emulsion formation mechanisms (Park and Anderson, 2012; Shum et al., 2010; Zhou et al., 2006). However, few researches have been done systematically on the sizes of the double-emulsion droplets, especially of the millimeter-scale ones.

In this work, we present a newly designed dual-coaxial capillaries device, which can be easily assembled or disassembled, for the production of double-emulsion droplets and emulsion-based millimeter-scale hollow polymer spheres. Two configurations of such devices were employed in the experimental work, where the difference lied in the relative locations of capillaries tips. Using these droplet generators, we studied the droplets generation and their sizes in detail, while special attention was paid to the comparison of the double-emulsion droplet size due to the difference of device configuration.

2. Experimental

2.1. Dual-coaxial capillaries microfluidic device

As shown in Fig. 1, the double-emulsion generator is composed of mainly two parts: one is the supporting body of the generator, manufactured of teflon to fix the capillaries coaxially; the other is the capillaries that the fluids flow through. The outer diameters of the inner capillary, the middle capillary and the collecting tube are exactly the same as the diameters of the vertical cylindrical holes of Part I, Part II and Part III of the supporting body, respectively. A steel capillary (i.d. = 0.2 mm, o.d. = 0.5 mm) acted as the inner channel is inserted into the vertical hole of Part I along its main axis. The middle capillary (i.d. = 0.8 mm, o.d. = 1.2 mm) is a glass one, whose wall is pretreated hydrophobic with n-octadecyltrimethoxysilane. The middle capillary is inserted into the hole of Part II, served as the channel of the middle phase. To visualize the generation of double emulsions, a transparent glass tube with inner diameter of 2.2 mm is used as the collecting tube (i.e., the outer channel). The three parts (I, II and III in Fig. 1) with capillaries fixed in their respective holes are assembled together coaxially, that is, forming the double-emulsion drops generator.

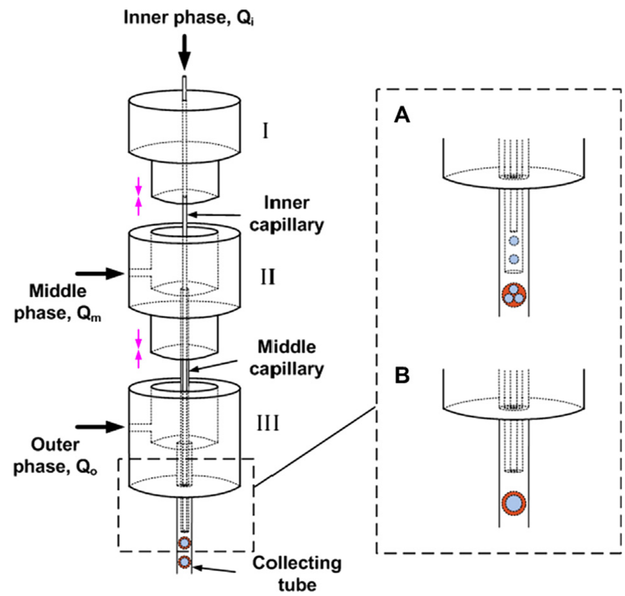

Fig. 1. Schematic of the dual co-axial capillaries device, where A is the two-step sub-type and B is the one-step sub-type of this device.

Two different devices are manufactured, where the difference is the relative position of the inner and middle capillaries′ ends. For the first one (in Fig. 1A), referred to as “two-step device”, the inner capillary end is located upstream to the middle capillary end; while for the second type (in Fig. 1B), referred to as “one-step device”, the inner capillary end is located at the same position of the middle capillary end. Three syringe pumps (Longer Pump, China) are used to deliver the inner fluid, the middle fluid and the outer fluid to the three capillaries, respectively, at certain liquid flow rates.

The dual-coaxial capillaries devices designed above are very convenient to be assembled, disassembled and washed up for re-use. Besides, many kinds of capillaries (glass, steel, teflon, silica, PEEK, etc.) could be selected for channels flexibly on demand. Single emulsion or double emulsions with high monodispersity could be generated using this kind of devices and their sizes could be adjusted by varying the liquid flow rates of the three streams of fluids.

2.2. Materials

A 2 wt% aqueous solution of polyvinyl alcohol (PVA, Mw 75,000, 88% hydrolyzed) (Aladdin, China) in deionized water is used as the outer continuous phase, W2. Polystyrene (PS, Mw 250,000) (Acros Organics, Belgium) dissolved in fluobenzene (FB) (Aladdin, China) at weight percentage of 10% is used as the middle oil phase, O. The inner phase, W1, is deionized water without any additives or an aqueous solution of 1 wt% sodium dodecyl sulfate (SDS).

2.3. Experimental procedure

After the dual-coaxial capillaries microfluidic device is assembled, the emulsions generator is fixed to an iron pole with its axis perpendicular to the experiment table. The droplet formation from co-flowing liquids in coaxial capillaries can be achieved either in dripping or jetting mode. However, as the sizes of droplets generated in jetting mode would be polydispersed due to the Rayleigh–Plateau instability (Utada et al., 2007), the experiments in this work are performed in dripping flow mode to ensure the formation of monodispersed emulsion drops.