Monodisperse and size-tunable high quality factor microsphere biolasers

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Abstract: We demonstrate a novel microfluidic-based fabrication of dye-doped protein nearly monodisperse microsphere biolasers with tunable size from 150 to 50 μm. In particular, for a 85 μm-microsphere series, about 70% of fabricated microspheres have the same size of 85 μm and the deviation of the rest microspheres is only 3 μm. Under optical pumping, the fabricated microspheres emit whispering gallery mode (WGM) lasing emission with a lasing threshold of 11 μJ mm^{-2} and quality factor up to 3000. Especially, microspheres with the same size exhibit similar lasing threshold and spectrum. The result indicates the high reproducibility of the microfluidic based fabrication technique. Our work provides an effective method for mass-production of high quality factor microsphere biolasers which is a significant step toward real biosensing and medical applications.

1. Introduction

Whispering gallery mode (WGM) microsphere biolasers have attracted a lot of attention due to their potential for biological applications such as biosensing, cell-tracking, and cell-imaging [1-4]. They feature a simple fabrication process but exhibit excellent laser properties including low lasing threshold and high-quality factor [5].

Several effective methods have been investigated for the fabrication of microsphere biolasers. For example, using the freeze-drying technique, Wei et al. obtained WGM granules laser from starch [6]. Basing on emulsions and dehydration of droplets in polydimethylsiloxane, Ta et al. fabricated dye-doped protein microsphere lasers [7]. Recently, we have demonstrated that protein dehydration is a fast and effective method for producing microspheres [8, 9]. However, all current techniques are unable to control effectively the size of microsphere lasers and fabricated microspheres are polydisperse with diameters ranging from a few to several hundred micrometers [6, 10]. These drawbacks hinder their potential applications.

Recently, microfluidic technology has emerged as a powerful tool for studying very small volume samples [11], manipulating micrometer-sized droplets [12-14]. It also exhibits advantages such as high efficiency (short time) in fabricating large numbers of monodisperse microlasers [15, 16]. Nevertheless, this technique has not been explored for making both droplet and solid-state microsphere biolasers. In this work, we demonstrate a unique technique that combines microfluidic channels with protein dehydration process for fabricating nearly monodisperse dye-doped protein microsphere biolasers with tunable size from 150 to 50 μm.

2. Experimental

Figure 1a illustrates the schematic fabrication of dye-doped protein microsphere lasers using microfluidic technology. The microfluidic device consists of four main parts: three input channels, intersection point, one output channel, and a collection container. It made of Norland Optical Adhesive 81 (NOA 81, from Norland Inc) and was created based on polydimethylsiloxane (PDMS, from Dow Corning) mold. The replica of PDMS mold from a dryfilm rigid mold is followed by the typical soft photolithography technique [17].

The middle input channel is 50 μm-width and 40 μm-depth. It is injected with Rhodamine B (RhB) doped bovin serum albumin (BSA, from Sigma-Aldrich) and it is used for discrete phase. Ratio RhB: BSA is 1% by weight and the concentration of BSA solution is 500 mg/mL). The two side input channels are 150 μm-width and 160 μm-depth. They are injected with 1-decanol (decanol, from Sigma-Aldrich) and they are used as a continuous phase. In this work, the injection rate of the discrete phase was fixed at 0.5 μL/min while the injection rate of the continuous phase changed from 1.5 to 6 μL/min. The output channel is 350 μm-width and 320 μm-depth. The collection container is 8 cm in diameter with a Teflon film on the bottom. Teflon is a hydrophobic material that helps to maintain droplets with spherical shapes.

Protein solution and decanol phases are driven into the microchannel at fixed volume flow rates. When they meet in the intersection point, the discrete phase thins gradually and break up into similar droplets due to the shear and squeezing forces exerted by the continuous phase. After that, droplets flow through the output channel as shown in a real system at Fig. 1b. The dehydration process begins immediately after droplets are formed. Due to the low solubility of decanol in water, the diffusion of decanol into droplets can be ignored [18]. In the end, solid-state microspheres are obtained in the collection container when most of the water molecules diffuse out of the droplets.

The shape and the surface morphology of fabricated microspheres were characterized by using a scanning electron microscope (SEM-TM4000plus-HITACHI). They were coated with a thin gold layer of about 10 nm thickness through a sputtering process prior to the SEM measurement. Optical properties of microspheres were investigated by a micro-photoluminescence (μ-PL) setup. The pumping source is a Nd: YAG nanosecond pulse laser (Litron lasers) with a wavelength of 532 nm, a repetition rate of 10 Hz, and a pulse duration of 7 ns. The microspheres were excited by a focus laser beam with a spot size of ~ 350 μm in diameter. Emission from them was then collected by a 10× objective and subsequently delivered to an AvaSpec-2048L (Avantes) for spectral recording. The spectral resolution is about 0.2 nm. All experiments were carried out in the air under ambient conditions.

Fig. 1. (a) Illustration of a microfluidic device used to fabricate dye-doped protein microdroplets. (b) Optical image of a real microfluidic chip showing the formation of monodisperse droplets.

3. Results and discussion

Figure 2 presents the size-tunable of microspheres as a function of the speed ratio of the two liquid phases. As the injection rating of decanol gradually rises from 1.5 to 6 μL/min, the "main" size of the microsphere decreased from 145 to 55 μm. This is understandable as the injection rate of the continuous phase increases, the squeezing forces exerted proportionally increases which results in larger energy to separate the liquid stream in the discrete phase into droplets and leading to a reduction in the size of the created droplets. It is suggested that our fabrication approach can be suitable for other kinds of biolasers based on aqueous solutions.

Fig. 2. The diameter of the microspheres expressed as a function of the rate ratio of the two liquid phases.

Figures 3 shows optical images and size distributions of 110 and 85 μm microsphere series. These microspheres were created when the rate ratio of two liquid phases V(decanol)/V(protein solution) equal to 5 and 6, respectively. From the optical microscope images, the microspheres exhibit similar sizes with spherical shapes (Fig. 3a and 3c). Regarding the size distribution, we have measured about 60 microspheres and the results present in Fig. 3b and 3d. About 50% of the spheres have the same diameter 110 μm (110 μm-bead) and 70% of the spheres have the same diameter of 85 μm (110 μm-bead). The variation of size is around only 3-4%. Fabricated microspheres exhibit spherical shape and smooth surface which are effective for optical confinement. It is confirmed by SEM image. For instance, the SEM image of the 110 μm-microsphere series is shown in Fig. 3e together with a higher magnification at Fig. 3f.

Fig. 3. (a) and (c) Optical microscope images of fabricated microspheres with a mean size of 110 and 85 μm, respectively. (b) and (d) are the size distribution of these microspheres, respectively. (e) Scanning electron microscope (SEM) image of microspheres with a diameter of 110 μm. (f) High magnification SEM of a typical "twin" microsphere.

Fabricated dye-doped protein microspheres can work as efficient lasers sources under optical pumping. PL spectra from an 85 μm-diameter sphere under different pumping energies of 0.78 and 2.14 μJ/pulse are plotted in Fig. 4a and 4b. At the lower pumping energy, the broad spontaneous emission is observed. However, when the pumping energy increases, lasing modes start to appear and they are well recognized at the 2.14 μJ/pulse. Moreover, the edge of the microsphere exhibits a higher brightness than the inner part which is the evidence of whispering gallery mode (WGM). The lasing threshold of 1.05 μJ per pulse can be determined by analyzing the integrated PL intensity as a function of pump pulse energy (Fig. 4c). This threshold is equivalent to a fluence of 10.92 μJ mm^{-2}. The quality (Q) factor of a lasing mode can be defined as $Q = \lambda/\delta\lambda$ (where $\delta\lambda$ is the full width at half maximum (FWHM) of the lasing mode) is about 3000. Both of lasing threshold and Q factor are comparable with some other kind of micro-bio-lasers [6, 8, 9].

It is expected those different microspheres but has the same size would have similar lasing properties. Figure 5a-5d show the laser spectrum of 4 different microspheres. Two of them have a diameter of 76 μm and two have a diameter of 85 μm. It can be seen that the lasing spectra of microspheres with the same diameter are very similar and the free spectral range (FSR) is the same (1.05 nm for the 76 μm spheres and 0.97 nm for the 110 μm spheres). The result indicates the high reproducibility of the microfluidic based fabrication technique. Similar results can be observed from microlasers fabricated by other techniques such as inkjet [19] or laser direct writing (LDW) [20]. However, this observation may be the first time in biolasers, especially microsphere biolasers.

FSR of the lasing spectrum is an important parameter and it is found that measured FSRs of fabricated microsphere biolasers are consistent with WGM theory. FSR can be estimated as $\lambda 2/\pi nD$, where λ is the lasing wavelength, n and D is the refractive index and diameter of the spheres. In our case $n = 1.47$, $D = 76$ and 85 μm. With assuming $\lambda = 620$ nm then the calculated FSRs are 1.06 and 0.97 nm which are well agreed with the experimental data of 1.05 and 0.97 nm, respectively.

Fig. 4. (a) and (b) PL spectra from an 85 μm-diameter sphere below and above the lasing threshold. The inserted images show the PL microscope image of the corresponding microsphere. All scale bars are 50 μm. (c) The corresponding integrated PL intensity of the sphere as a function of pump pulse energy.

Fig. 5. (a) and (b) diameter of 76 μm. (c) and (d) diameter of 85 μm. Pumping energy was 2.14 μJ for all microspheres. All scale bars are 50 μm.

4. Conclusions

We have demonstrated that microsphere biolasers with narrow size distribution can be fabricated by combining protein dehydration with a microfluidic device. Furthermore, the diameter of the laser microsphere can be controlled flexibly in the range of 50 to 150 micrometers. Under optical pumping, these microspheres can work as efficient laser sources with a low lasing threshold of 11 $\mu J\ mm^{-2}$ and Q factor of 3000. Microspheres with the same diameter exhibit very similar lasing spectrum which indicates the reproducibility of the fabrication technique. These microsphere biolasers can be mass-produced and they are good candidates for biosensing and medical applications.

5. Funding

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.99-2017.65.

References