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Original Article

Fabricating Microsphere Lasers by Protein Dehydration: A Fast Fabrication Method and Excellent Lasing Properties

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Abstract: Microsphere biolasers have attracted a great deal of interest due to their potential in biosensing and cell-tracking. Various fabrication techniques have been explored for making microsphere biolasers, such as freeze-drying in a vacuum, standard oil in water dispersion procedure and protein dehydration in a solvent. The protein dehydration is highly interesting due to its simplicity and fast processing time. In this work, we demonstrate the fabrication of microsphere biolasers using protein dehydration in decanol and demonstrate that the fabrication process can speed up if the solvent is heated. When the solvent is heated to 60 °C, the fabrication time is reduced to half compared with the case when the sample is made at room temperature. Interestingly, while heating the solvent helps to decrease the fabrication time, it does not affect the lasing properties of the samples. The lasing thresholds of microsphere biolasers fabricated at 25 °C and 60 °C are similar. Furthermore, lasing operation under continuous pumping and lasing stability against storing time are also investigated. A typical 42 µm microsphere can still lase upon 2×10^4 excitation pulses. Lasers can work well after being stored for 12 weeks under ambient conditions.

Keywords: Whispering gallery mode, biolaser, protein dehydration, microsphere laser.

1. Introduction

Whispering gallery mode (WGM) biolasers have attracted considerable attention due to their potential for applications in biophotonic fields [1-4]. In a WGM cavity, light is trapped inside and

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enhanced by multiple total internal reflections at the interface between the cavity and surrounding medium. Some structures of WGM cavities such as microsphere, microhemisphere, microdisk, microtoroid were investigated [5-7]. Among them, microsphere is a very interesting case due to its simple fabrication, low lasing threshold and promising for ultra-sensitive sensors [8-10].

Recently, several techniques have been studied to fabricate microsphere biolasers such as freeze-drying vacuum, slow solvent evaporation, emulsions and dehydration of droplets in polydimethylsiloxane (PDMS) [11-13]. These methods are very effective in making microsphere lasers but there is a disadvantage that they are time-consuming. The fabrication process can take several to 12 hours. To solve this issue, we have proposed a unique technique - protein dehydration as a very fast method for making protein-based microsphere lasers [14-16]. Using this technique, dye-doped protein droplets (from natural egg white or bovine serin albumin) can be turned into solid spheres by the diffusion of water molecules inside the droplet to the appropriated outer environment (decanol). Generally, the fabrication process takes only 10 minutes.

In this report, we show that the fabrication time can be further decreased by increasing the solvent (decanol) temperature. While heating the solvent helps to decrease the fabrication time, it does not affect the lasing properties of the samples. In addition, the influence of storage time and long-time pumping on lasing performance is also investigated.

2. Materials and Methods

Bovine serin albumin (BSA, ≥ 98% purity), Rhodamine (RhB, ≥ 95% dye), and decanol (≥ 99% purity) were purchased from Sigma-Aldrich. Pure BSA solution was prepared by dissolving 0.5 g of BSA in 0.5 mL deionized water. Dye was added by mixing 0.5 mL RhB solution 1 wt% with the above BSA solution.

The protein-dehydration method that was demonstrated in our previous publications [14, 15] was used to fabricate microsphere biolasers. The working principle of this method is shown in Figure 1. Dye-doped BSA droplets are created into decanol (Figure 1a). Then, the dehydration process happens spontaneously in which water molecules diffuse into decanol (Figure 1b). It is noted that the diffusion of protein and RhB to decanol is negligible. As a result, droplets shrink and become solid microspheres when all water molecules are completely diffused to decanol (Figure 1c).

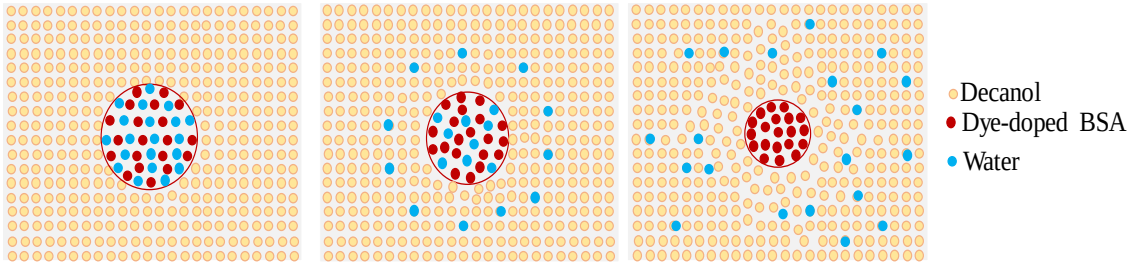

Figure 1. Illustration of the protein dehydration process.

In this work, the temperature of the outer medium (decanol) was heated and the result shows that the fabrication time can be reduced compared with our previous work in which the fabrication process was carried out at room temperature. As shown in Figure 2, a sensor receives the temperature signals of the decanol and sends them to a control block of the heater. As a result, the temperature of the decanol can be set to be exactly at 25 °C, 40 °C, 50 °C and 60 °C. A digital optical microscope (connected with

a laptop) with a magnification of 20× was used to monitor the formation of microspheres. The dehydration process of droplets was captured automatically and continuously after equal intervals of 6 s. The changing of droplets' diameter was calculated by using MATLAB software.

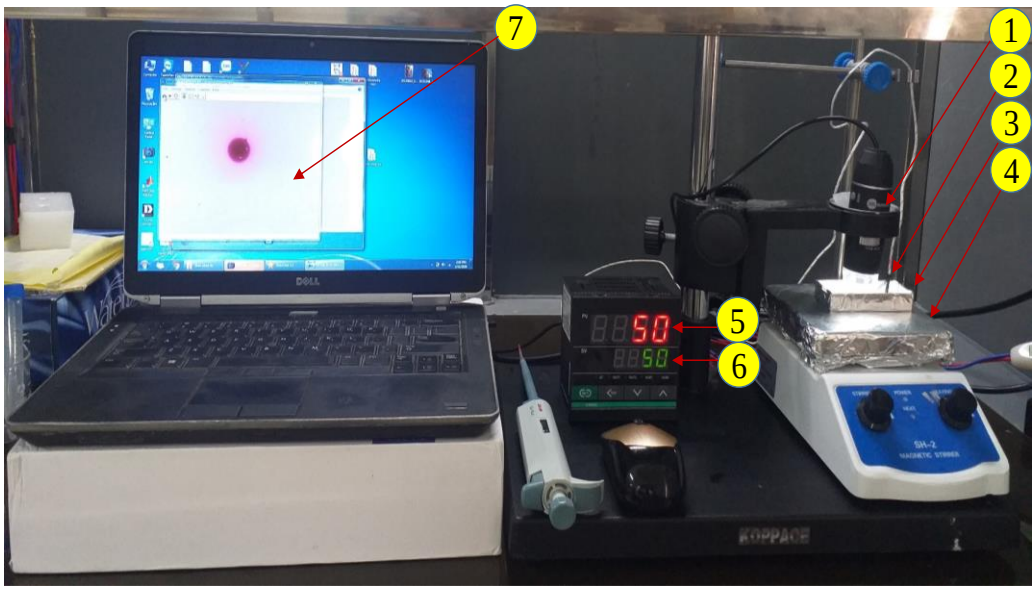

Figure 2. Components used to study the dehydration process of a single droplet in decanol: 1. Digital optical microscope; 2. Temperature sensor; 3. Teflon box containing decanol; 4. Heater; 5. Set the temperature; 6. Real temperature of the decanol; 7. Optical microscope image of a droplet during the dehydration process.

The optical properties of the fabricated microspheres were studied 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. All microspheres were stored in a refrigerator at 5 °C. Before making optical measurements (in ambient air and at room temperature) they were dried at 40 °C for 10 minutes.

3. Results and Discussion

3.1. The Influence of Decanol Temperature on the Dehydration Process

To study the influence of temperature on the dehydration process, we fixed the initial BSA concentration and droplet size. Four droplets with an initial size of about 124 μm are studied. It is observed clearly that increasing the temperature of decanol significantly shortens the fabrication time of dye-doped microspheres (Figure 3a). As shown in the inset, it takes about 380 s to complete the dehydration process (solid microsphere of about 84 μm is formed) at room temperature (25 °C), but it reduces to 324 s (at 40 °C) and reaches a minimum of 210 s at 60 °C. This is understandable because when the temperature increases the diffusion rate of water to decanol should also increase, which reduces the dehydration time. As mentioned above, the diffusion of dye molecules to decanol is negligible. As

shown in Figure 3b, the colour of the droplet is maintained during the dehydration process until a solid sphere is formed.

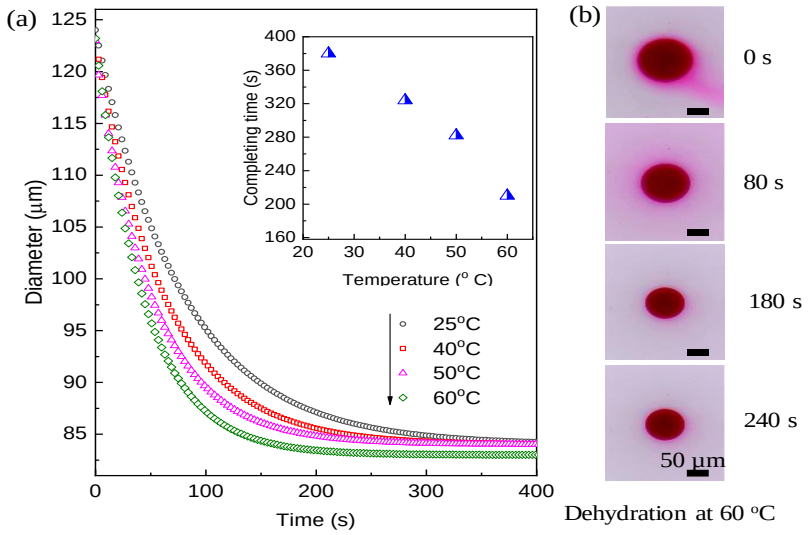

Figure 3. a) The influence of decanol temperature on the dehydration process;
The inset shows the completed hydration time as a function of temperature;
b) Optical microscope images of a typical dye-doped droplet during the dehydration process.

3.2. Optical Microscope and Sem Images of Fabricated Microspheres

Figure 4a shows the optical microscope of dye-doped BSA microspheres. Their sizes are about 10 to 100 µm. Their surface morphologies were studied by a scanning electron microscope (SEM, TM4000plus-HITACHI). It indicates that microspheres have smooth surfaces which are necessary for high quality factor optical resonators.

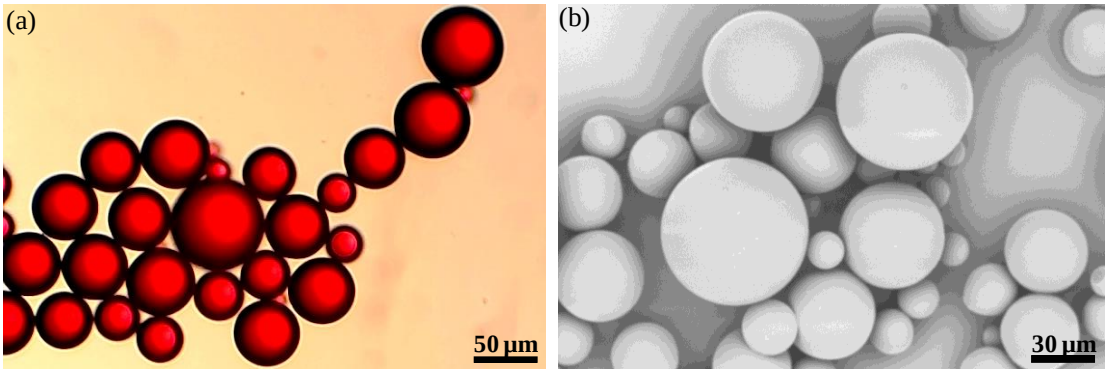

Figure 4. a) Optical microscope image and b) scanning electron microscope image
of dye-doped protein microspheres.

3.3. Influence of Solvent Temperature on the Lasing Threshold

Fabricated microspheres can work as excellent microlasers. Figure 5a shows that the PL intensity of a single 40 µm-diameter microsphere (dehydration at 60 °C) increases with increasing pump pulse

energy (PPE) of the incident pumping laser, and lasing emission is observed when PPE = 2.14 μJ per pulse. The lasing modes (with sharp peaks) appear clearly in the wavelength ranging from 615 to 640 nm. Besides, the integrated PL intensity shown in Figure 5b indicates a nonlinear increase of the emission intensity supports the lasing action. A lasing threshold of 1.45 μJ per pulse was obtained. This value is comparable with the previous reports [14, 16].

Interestingly, while heating the solvent helps to decrease the fabrication time, it does not affect the lasing properties of the samples. As shown in Figure 5c, the temperature does not significantly change the laser emission threshold of microspheres and this is true for various sizes. In addition, it can be seen that as the size increases, the laser threshold tends to decrease gradually. It is because larger microspheres are supposed to have higher quality (Q) factor and thus, they can provide better optical confinement for the laser generation.

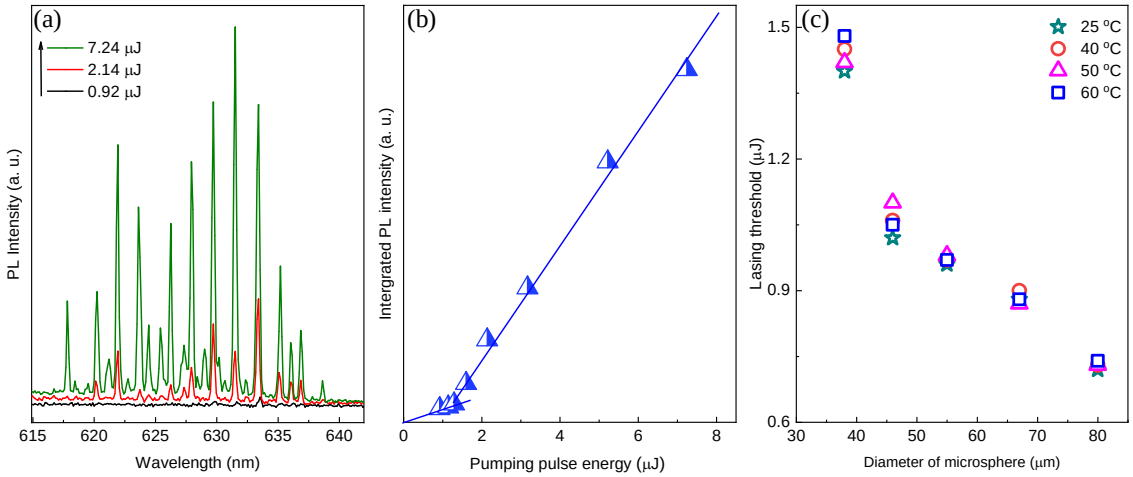

Figure 5. a) PL emission of 40 μm microsphere laser under different excitation pulse energies;
b) Integrated PL intensity of the microsphere laser versus pulse energies;
c) Lasing thresholds of five microspheres with various sizes fabricated at 25 °C, 40 °C, 50 °C and 60 °C.

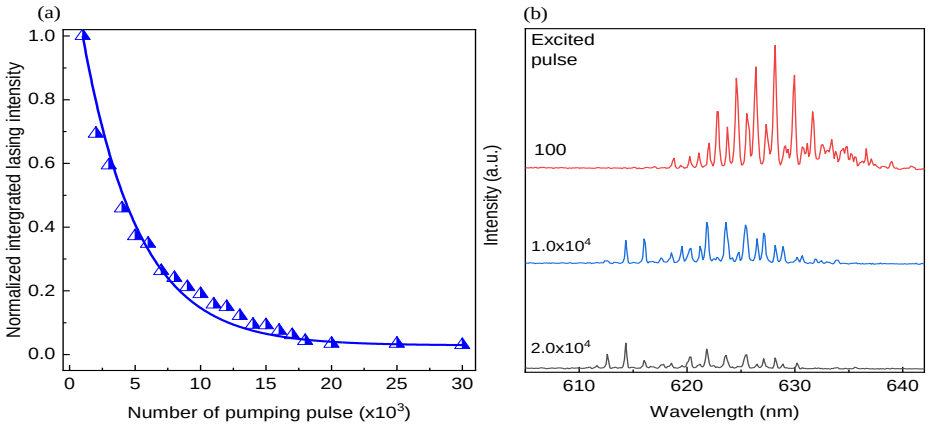

Figure 6. a) PL integrated lasing intensity of a 42 μm microsphere versus several pumping pulses;
b) Lasing spectrum of the sphere under different pumping pulses.

3.4. The Stability of Microsphere Biolasers under Continuous Pulse Excitation

Laser lifetime under continuous pulse excitations is an important parameter of a laser. Figure 6a shows the normalized integrated lasing intensity of a 42 µm microsphere as a function of the number of exciting pump pulses. Under excitation pulses of 2.14 µJ, the laser still lases after 3×10^4 pump pulses. In particular, the integrated lasing intensity decreased by 30% after about 2,500 pulses, 70% after 6,500 pulses, and 90% after 12,500 pulses. In addition, laser modes move to shorter wavelength regions with increasing pump pulses. The wavelength shift behaviour is due to the oxidation of dye molecules under long-term excitation [17].

3.5. The Influence of Storage Time on Lasing Properties of Microsphere Biolasers

It is necessary for a microsphere laser to operate stably over a long storage time. In Figure 7a, it can be seen that the mode positions of a laser microsphere (45 µm) are unchanged after a 12-week storage. During this time, the threshold of laser output tends to increase slightly, from about 1.60 µJ to 2.06 µJ (Figure 7b) and the integrated lasing intensity decreases by only 10% (Figure 7c). These results indicate that the microsphere laser can operate for a long time under normal storage conditions.

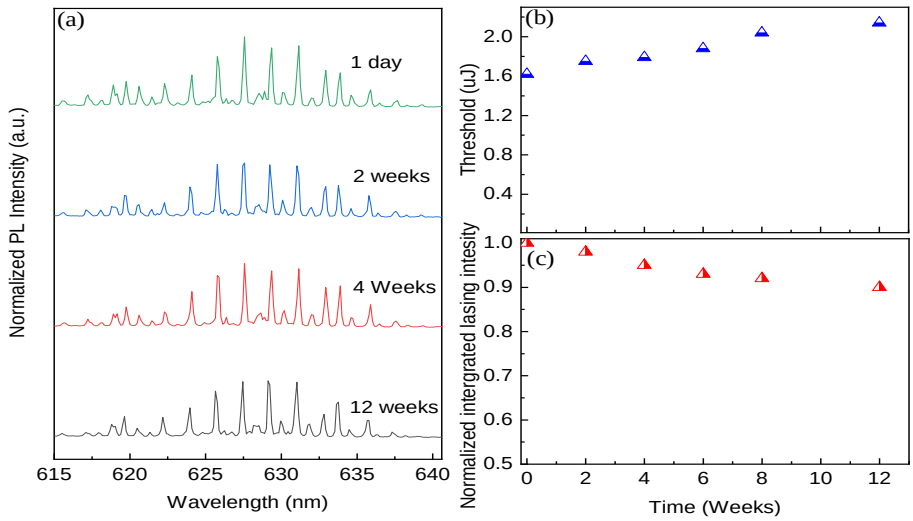

Figure 7. a) PL spectra of 45 µm microsphere lasers (under excitation energy of 2.14 µJ) at different storage times; b) Variation of lasing threshold; and c) PL integrated lasing intensity with storage time.

4. Conclusion

We have demonstrated an improved protein dehydration method for the fabrication of protein-based microsphere lasers. By increasing the solvent temperature, the fabrication time is shortened significantly without affecting the laser properties. Moreover, the results show that the microsphere laser can operate for a long time under normal storage conditions and after thousands of cycles of laser excitation pulses. Our work is significant for the development of biolasers, especially in the mass production of microsphere biolasers, which is a further step to employing microsphere lasers in biosensing and cell-tracking.

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References

[1] F. Vollmer, S. Arnold, Whispering-Gallery-Mode Biosensing: Label-free Detection Down to Single Molecules, Nat. Methods, Vol. 5, No. 7, 2008, pp. 591-596, https://doi.org/10.1038/nmeth.1221.

[2] J. Ward, O. Benson, WGM Microresonators: Sensing, Lasing and Fundamental Optics with Microspheres, Laser Photon. Rev., Vol. 5, No. 4, 2011, pp. 553-570, https://doi.org/10.1002/lpor.201000025.

[3] V. D. Ta, Y. Wang, H. Sun, Microlasers Enabled by Soft-Matter Technology, Adv. Opt. Mater, Vol. 7, No. 17, 2019, pp. 1900057, https://doi.org/10.1002/adom.201900057.

[4] D. Venkatakrishnarao, E. A. Mamonov, T. V. Murzina, R. Chandrasekar, Advanced Organic and Polymer Whispering-Gallery-Mode Microresonators for Enhanced Nonlinear Optical Light, Adv. Opt. Mater, Vol. 6, No. 18, 2018, pp. 1800343, https://doi.org/10.1002/adom.201800343.

[5] J. C. Long, H. W. Chan, A. B. Churnside, E. A. Gulbis, M. C. Varney, J. C. Price, Ultra-high-Q toroid Microcavity on a Chip, Nature, Vol. 421, No. 6926, 2003, pp. 922-925, https://doi.org/10.1038/nature01371.

[6] M. Humar, S. Hyun Yun, Intracellular Microlasers, Nat. Photonics, Vol. 9, No. 9, 2015, pp. 572-576, https://doi.org/10.1038/nphoton.2015.129.

[7] V. D. Ta, R. Chen, H. D. Sun, Self-Assembled Flexible Microlasers, Adv. Mater, Vol. 24, No. 10, 2012, pp. 60-64, https://doi.org/10.1002/adma.201103409.

[8] G. C. Righini, S. Soria, Biosensing by WGM Microspherical Resonators, Sensors, Vol. 16, No. 6, 2016, pp. 905, https://doi.org/10.3390/s16060905.

[9] V. D. Ta, R. Chen, D. M. Nguyen, H. D. Sun, Application of Self-Assembled Hemispherical Microlasers As Gas Sensors, Appl. Phys. Lett, Vol. 102, No. 3, 2012, pp. 031107, https://doi.org/10.1063/1.4788751.

[10] T. Reynolds, N. Riesen, A. Meldrum, X. Fan, J. M. M. Hall, T. M. Monro, A. François, Fluorescent and lasing Whispering Gallery Mode Microresonators For Sensing Applications, Laser Photon. Rev., Vol. 11, No. 2, 2017, pp. 1600265, https://doi.org/10.1002/lpor.201600265.

[11] D. Venkatakrishnarao, M. A. Mohiddon, R. Chandrasekar, The Photonic Side of Curcumin: Microsphere Resonators Self-Assembled from Curcumin Derivatives Emitting Visible/Near-Infrared Light, Adv. Opt. Mater, Vol. 5, No. 2, 2017, pp. 1600613, https://doi.org/10.1002/adom.201600613.

[12] Y. Wei, X. Lin, C. Wei, W. Zhang, Y. Yan, Y. S. Zhao, Starch-Based Biological Microlasers, ACS nano, Vol. 11, No. 1, 2017, pp. 597-602, https://doi.org/10.1021/acsnano.6b06772.

[13] V. D. Ta, S. Caixeiro, F. M. Fernandes, R. Sapienza, Microsphere Solid-State Biolasers, Adv. Opt. Mater, Vol. 5, No. 8, 2017, pp. 1601022, https://doi.org/10.1002/adom.201601022.

[14] T. V. Nguyen, N. V. Pham, H. H. Mai, D. C. Duong, H. H. Le, R. Sapienza, V. D. Ta, Protein-based Microsphere Biolasers Fabricated by Dehydration, Soft Matter, Vol. 15, No. 47, 2019, pp. 9721-9726, https://doi.org/10.1039/C9SM01610D.

[15] T. V. Nguyen, H. H. Mai, T. V. Nguyen, D. C. Duong, V. D. Ta, Egg White Based Biological Microlasers, J. Phys. D: Appl. Phys, Vol. 53, No. 44, 2020, pp. 445104, https://doi.org/10.1088/1361-6463/ab9bbe.

[16] T. V. Nguyen, V. D. Ta, High-quality Factor, Biological Microsphere and Microhemisphere Lasers Fabricated by a Single Solution Process, Opt. Commun., Vol. 465, 2020, pp. 125647, https://doi.org/10.1016/j.optcom.2020.125647.

[17] H. J. Moon, Y. T. Chough, J. B. Kim, K. An, J. Yi, J. Lee, Cavity-Q-driven Spectral Shift in A Cylindrical Whispering-gallery-mode Microcavity Laser, Appl. Phys. Lett, Vol. 76, No. 25, 2000, pp. 3679-3681, https://doi.org/10.1063/1.126747.