STARCH BASED MICROSPHERE BIOLASERS

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DOI: 10.56651/lqdtu.jst.v1.n01.627.pce

Abstract

Recently, biolasers whose optical cavity is made of natural materials such as serum-extracted protein, egg white, cellulose, and gelatin have attracted a lot of attention. The advantage of these lasers is their biocompatibility and biodegradability which is significant for biointegration. In this study, we demonstrate that starch is a low-cost and good material for microsphere biolasers. By using a simple emulsion method with a dehydration process, dye-doped starch microsphere lasers with diameters ranging from 40 to 180 µm have been successfully obtained. Lasing properties are investigated and the results show that the lasing threshold is approximately 1.0 µJ and the quality factor can reach 2700. The starch-based microsphere lasers indicate excellent stability after a storage time of a month; thus, they are promising for practical applications in biological and chemical sensors.

Keywords: *Microsphere laser; starch; WGM laser.*

1. Introduction

For thousands of years, starches have been one of the most important foods providing nutrition and energy for human life [1-5]. In addition, starches are represented as a natural polymer with many applications in the fields of biomedicine and photonics [6, 7]. Starches have several interesting properties such as biocompatibility, flexibility, and good transmittance in the visible region which make them an excellent candidate for the fabrication of biolasers [8-10].

Biolasers rely on various cavity structures such as the random scattering medium, Fabry-Perot and whispering gallery mode (WGM) cavities. Among those alternatives, WGM laser is an interesting case due to its simple fabrication, high quality (Q) factor, and low lasing threshold [11-13]. Several WGM microlasers from different biological materials have been reported including protein microdisk and microsphere lasers [14-16], egg white based microsphere lasers, potato starch based microellipsoid lasers [17, 18]. Furthermore, these biolasers have been employed as temperature sensors [20, 21]. However, there are

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some disadvantages in the fabrication of biolaser such as: requirement for a complicated process [14], long fabrication time (up to 12 hours), or low temperature (-50°C) requirement [18],... leading to difficulties in massive fabrication of biolaser. In addition, the stable operation and durability of this kind of lasers have not been studied.

Therefore, in this study, we aim to develop a simple and fast process to fabricate WGM microsphere lasers based on starches. Based on the dehydration process, we report an efficient method for the massive fabrication of low-cost dye-doped WGM microsphere lasers from starches (Kudzu).

2. Experiment

2.1. Preparation of dye-doped starch solution

First, 1 g of starch powder (Kudzu, which was purchased from Bimall, Hanoi, Vietnam; 500 g/box) was put into a cup (made of Teflon). Subsequently, 3 mL of deionized water was added. The mixture was stirred and heated at 90°C for 6 minutes to obtain the uniform solution, then allowed to cool down naturally. Next, 0.5 mL of Rhodamine B aqueous solution 2 wt% was added and stirred for 3 minutes to obtain a homogeneous dye-doped starch solution.

2.2. Fabrication of starch-based biolasers

As shown in Fig. 1a, a micropipette was used to create a dye-doped starch droplet (from the solution above) inside polydimethylsiloxane (PDMS - purchased from Sigma). This droplet was then dispersed into numerous smaller droplets (Fig. 1b). Since the starch solution and PDMS do not dissolve into each other, as a result, the spherical droplets were obtained. After that, these droplets were heated at 100°C for 6 minutes to evaporate all the water molecules and solidify. Finally, the PDMS was removed by using ethyl acetate (Fig. 1c). The fabricated solid-state microspheres were then placed on glass substrates (Fig. 1d) and marked their positions for convenience when studying their shape and optical properties.

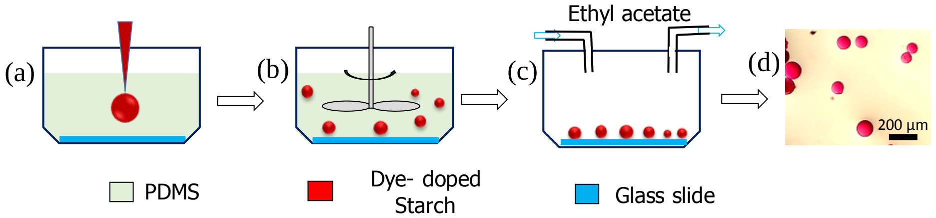

Fig. 1. Illustrating the fabrication process of dye-doped starch microspheres.

2.3. Shape and optical characterization

The shape and surface of fabricated microspheres were studied by using scanning electron microscope (SEM-TM4000plus-HITACHI) after they were coated with a thin gold layer of about 10 nm thickness by sputtering.

The optical properties of microspheres were investigated by using 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. Individual 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 delivered to an AvaSpec-2048L (Avantes) for spectral recording. The spectral resolution is about 0.2 nm.

3. Results and discussions

3.1. Dye-doped starch microspheres

The dehydration process dehydrated most of the water molecules out of the dye-doped starch droplets and solid-state microspheres were subsequently obtained, the time of sample making is about 12-15 minutes, approximately 1/60 times of WGM lasers from potato starches. This result shows the effectiveness of the method. Fig. 2 shows the shape and size distribution of the fabricated microsphere clusters. Fig. 2a presents a SEM image of microspheres and a high magnification of a single microsphere (about 125 µm in diameter in the inserted image), demonstrating a quite smooth surface which is suitable for a high-quality WGM laser source. The size distribution of a random group of 38 microspheres was statisticallly shown in Fig. 2b. About 65% of them have a diameter in the 70-120 µm range, and several microspheres with similar size were obtained in the 80, 95, 100, and 112 µm regions. Smaller microspheres can be obtained with a more dilute starch solution or increased droplet agitation [16]. It is also possible to control the microsphere size if combined with a microfluidic channel or droplet printing system [19, 22-24].

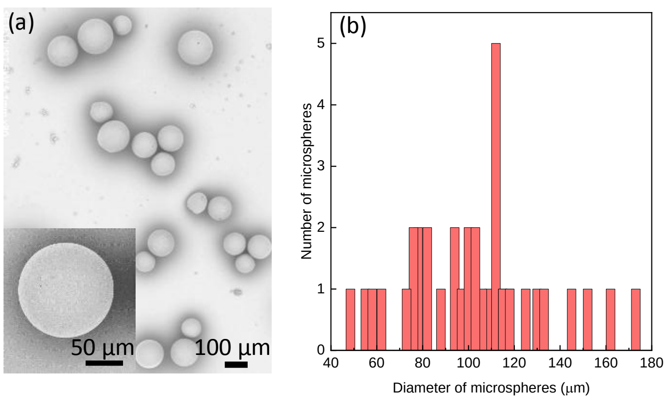

Fig. 2. (a) Scanning electron microscopy images of dye-doped starch microspheres; (b) Size distribution of 38 random fabricated microspheres.

3.2. Lasing properties of starch-based microsphere lasers

The dye-doped starch microspheres can work as efficient laser sources under optical pumping. Under a low pump pulse energy (PPE) such as 0.5 µJ, only broad emission with weak intensity is observed (from 49 µm-diameter microsphere, Fig. 3). However, when the pump pulse energy reaches about 1.0 µJ, 04 low-intensity laser modes begin to appear. The maximum intensity mode reaches 1620 (a.u.). These modes have a nonlinear increase in intensity with the increase of PPE: almost 5 times - reaching about 8,300 (a.u.) when the PPE increases by 1.3 times (1.0 to 1.3 µJ) and up to 12 times when the PPE is increased to 1.8 µJ. The nonlinear dependence of output intensity with PPE indicates the lasing threshold is about 1.0 µJ, which is comparable to the protein microsphere lasers [14], and about 3 times higher than the WGM ellipsoid lasers [18].

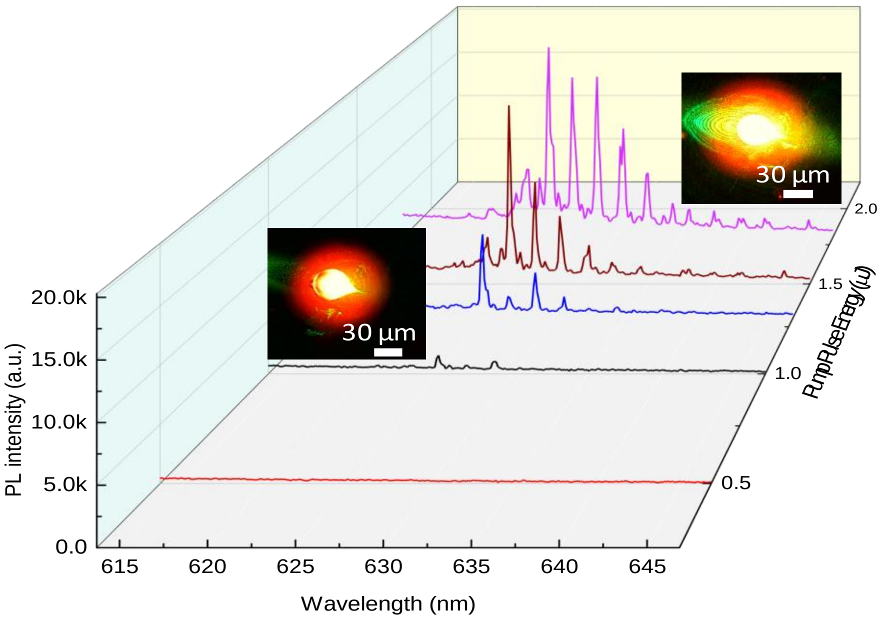

Fig. 3. The lasing mode intensity of the microsphere is a function of pump pulse energy.

The free spectral range (FSR) of lasing modes can be calculated from the lasing spectrum of different sizes as shown in Fig. 4. Particularly, Fig. 4a presents the lasing spectrum from a 49 µm-diameter microsphere (under PPE = 1.8 µJ), FSR is calculated at 1.80 nm, while with D = 88 µm, FSR can be determined to be 0.98 nm (Fig. 4b). Furthermore, we have studied a number of microspheres with different sizes and their FSRs are plotted in Fig. 4c which shows FSRs as a linear function of 1/D. This result is consistent with the theory of WGM lasers, where FSR can be estimated as [11]:

$$FSR = \left(\frac{\lambda^2}{\pi n}\right)\frac{1}{D}$$

where λ, n, and D are the lasing wavelength, refractive index, and diameter of the microsphere, respectively. In this study, the microspheres are fabricated with the same material and process, so the refractive index n can be considered equivalent, while most of the lasing modes appear in the region of 615-645 nm.

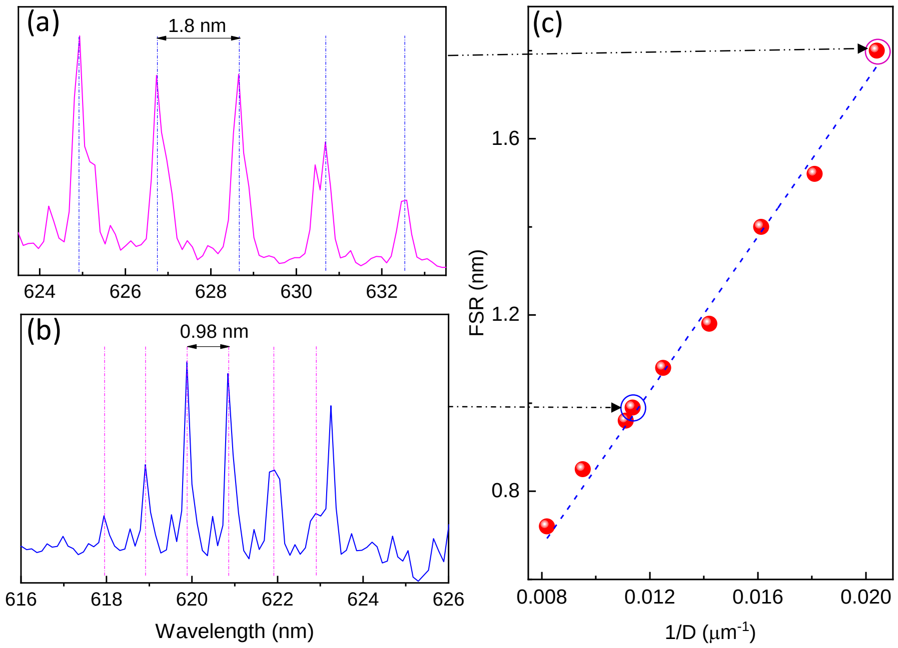

Fig. 4. (a) & (b) Lasing spectrum of 49 and 88 μm diamter microspheres, (c) FSR theoretical calculation and experimental results of 9 microspheres.

The size-dependent Q characteristics of the dye-doped microspheres were also studied. Figures 5a and 5b show the profile of a typical lasing mode in the range of 2.7 nm of two different microspheres.

It can be seen that the spectral linewidth of a 49 μm-diameter microsphere is 0.36 nm, which is 1.33 times larger compared with that of 0.27 nm of an 88 μm-diameter microsphere. In general, a larger microsphere exhibits narrower lasing modes compared with a smaller one. The Q factor of a lasing mode feature can be defined as Q = $\lambda/\delta\lambda$, thus corresponding values of Q factor are about 1,650 for the 49 μm-diameter microsphere and 2,260 for the 88 μm-diameter microsphere. Fig. 5 indicates that the Q factor is found to increase with the diameter of microsphere, which can be explained that the increase in diameter of microsphere means the increase in both cavity length (L), and reflectivity (R) at the microsphere-air interface. These two factors push the Q factor up based on the following equation Q = $2\pi nL/\lambda(1-R)$. The Q factor of our dye-doped starch microsphere biolasers can be comparable with protein-based microsphere (31.5 μm-diameter microsphere, Q factor ≈ 3000) and microdisk lasers (40 µm-diameter microdisk, Q factor ≈ 2400) fabricated using different methods [14, 25].

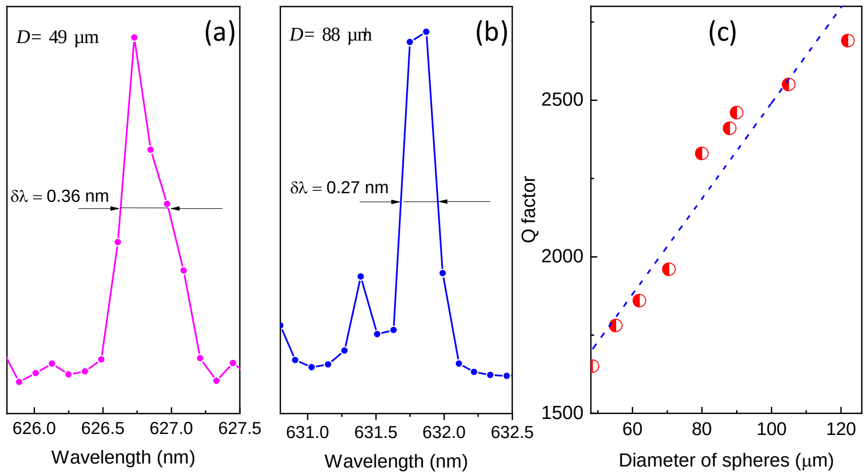

Fig. 5. (a) & (b) Spectral linewidth of 49 µm and 88 µm-diameter microspheres, respectively; (c) Q factor as a function of microsphere diameter.

The fabricated microsphere biolasers can operate stably over a long storage time. In Fig. 6, it can be seen that the mode positions (49 µm microsphere) are unchanged after storage for 4 weeks. Moreover, during this time its threshold and Q factor also tend to remain unchanged. These results indicate that the microsphere laser can work for a long time under normal storage conditions (all microspheres were stored at about 4°C in the refrigerator).

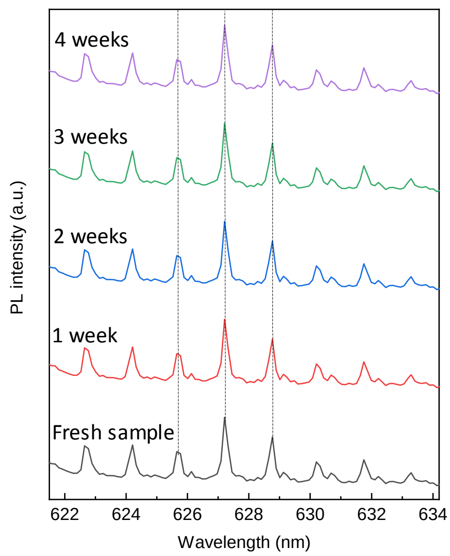

Fig. 6. The lasing spectrum 49 µm microsphere lasers (under excitation energy of 1.80 µJ) at different storage times.

4. Conclusion

We have demonstrated that Kudzu starch is a good biomaterial for a microsphere laser. By doping RhB into starch solution and using a simple dehydration process, microspheres with a diameter ranging from 40 to 180 µm are obtained. Under optical pulse excitation, these microspheres can operate as high-quality lasers with the lasing threshold as low as 1.0 µJ. The Q factor can be reached 2,700. Size-dependence of FSR characteristics is studied and show good agreement with the WGM theory. Our microsphere biolasers have potential applications in biological and chemical sensors.

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VI LASER SINH HỌC TỪ VẬT LIỆU TINH BỘT

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Tóm tắt: Gần đây, các nguồn laser sinh học có buồng cộng hưởng được làm từ vật liệu tự nhiên như protein chiết xuất từ huyết thanh, lòng trắng trứng, cellulose và gelatin,... đã thu hút được nhiều sự quan tâm chú ý. Ưu điểm của chúng là tính tương thích sinh học và phân hủy sinh học nên chúng có thể được tích hợp lên các đối tượng sinh học khác nhau. Trong nghiên cứu này, chúng tôi chứng minh rằng tinh bột là một vật liệu sinh học phù hợp, chi phí thấp để chế tạo các laser vi cầu chất lượng cao. Bằng cách sử dụng phương pháp đơn giản dựa trên hiện tượng nhũ tương với quá trình khử nước, các laser vi cầu từ tinh bột pha tạp hoạt chất màu đã được chế tạo thành công với đường kính nằm trong khoảng từ 40 đến 180 µm. Các đặc tính laser cho thấy ngưỡng phát xấp xỉ 1,0 µJ và hệ số chất lượng có thể đạt tới 2700. Bên cạnh đó, laser vi cầu hoạt ổn định sau khoảng thời gian một tháng cất giữ ở điều kiện thông thường nên chúng đủ bền cho một số ứng dụng tiềm năng trong cảm biến sinh học và hóa học.

Từ khóa: *Laser vi cầu; tinh bột; WGM laser.*

Received: 13/02/2023; Revised: 24/03/2023; Accepted: 20/04/2023; Published: 27/04/2023

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