Preparation of Spherical Particles by Vibrating Orifice Technique

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ABSTRACT

Preparation of micrometer-sized spherical particles containing Rhodamine 6G (R6G) has been investigated for the spherical cavity micro-laser. Using phenyl triethoxy silane (PTES) as a starting material, R6G-doped monodisperse spherical particles were prepared by the vibrating orifice technique. Processing is consist of two major processes: (1) Hydrolysis and polymerization of PTES and (2) Droplet formation from PTES oligomers by vibrating orifice technique. A cylindrical liquid jet (PTES oligomer and R6G diluted with alcohol) passing through the orifice of 10 and 20 μm in diameter breaks up into equal-sized droplets by mechanical vibration. Alcohol solvent of these droplets was evaporated during flying with carrier gas and subsequently solidified in ammonium water trap. For making smooth surface and good shaped particles, control of molecular weight of PTES oligomer was essential. R6G-doped hybrid spherical particles of 4 ~10 μm size of cavity structure were successfully obtained. The spherical particles were pumped by a second harmonic pulse of Q-switched Nd-YAG laser (532 nm wavelength) and laser emission peaks were observed at wavelengths which correspond to the resonance modes.

Keyword: Spherical cavity, Organic-inorganic hybrid matrix, Hydrophilic-hydrophobic property, Dye-doped spherical particles, Vibrating orifice technique, Laser emission.

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1. INTRODUCTION

Encapsulation of light in a cavity has been a stimulated interest for various optical devices. Fabry-Perot type cavity have been developed to conventional lasers. Encapsulation of light into a core-clad structure of a waveguide enables us to develop optical fibers for propagating of light. Recently, there has been considerable interest in a spherical cavity of micrometer size for its potential uses such as a light source of near-field scanning optical microscopy [1], components of photonic crystals [2], a low-threshold laser [3] and so on.
Strong interaction between laser light and a micrometer-size spherical particle causes an optical resonance in its inside since a spherical wall acts as a mirror. Using the resonance of a sphere lasing can be achieved at much lower excitation intensity than within the corresponding bulk materials [3]. Lasing on the resonance modes of various spherical particles containing a laser dyes has been demonstrated: 60 μm in diameter ethanol droplet containing Rhodamine 6G (R6G) [4], 10~20 μm plastic particles containing laser dyes [5,6]. Recently, we have made R6G-doped spherical particles of organic-inorganic materials by sol-gel technique (the emulsion technique). By the technique, particles of various sizes from submicron to several ten micrometer were made at once. Particles of 4~6 μm in diameter were selected and from them, a strong laser emission peak at 598 nm was confirmed by pumping a laser light of 532 nm wavelength with a second harmonic pulse of Q-switched Nd-YAG laser [7].

For preparing dye-doped inorganic spherical particles, various sol-gel techniques have been investigated by many authors [8,9]. Incorporation of organic laser dyes of relatively hydrophobic property such as R6G into inorganic particles, however, was very difficult [10]. In the previous work, we reported that particles can be successfully made from phenyltriethoxysilane (PTES) as a starting material and their matrix containing phenyl group in -Si-O-Si- structure was suitable to incorporate organic dyes into them [7]. Unfortunately, however, by the emulsion technique, particles of pore-free and desirable diameter were less than 5 % of the weight of as-prepared samples [11]. Although the potentiality of the dye-doped particles for spherical laser was shown, establishment of the controllability of particle diameter and homogeneity is inevitable for the applications.

Quality factor of the cavity strongly depends on size of spherical particles: Q value decreases with decreasing the size. Thus lasing is more difficult in small-size particles than those of large-size. On the other hand, lasing with no threshold is expected in wavelength-order size particles. Therefore, preparation of several micrometer-sized spherical particles is the first target of the study.

In this paper, by aiming at preparing monodispersed several micrometer-sized spherical particles, the vibrating orifice technique is developed. Optical properties of the dye-doped spherical particles, involving a lasing demonstration and its photodegradation, are also described.

2. EXPERIMENTAL PROCEDURES

Processing steps for preparing R6G-doped spherical particles are shown in Fig. 1. The fabrication is consisted of two major processes; (a) hydrolysis and polymerization of starting material, phenyltriethoxy silane (PTES), and (b) particle formation by vibrating orifice technique followed by solidification in ammonia water.

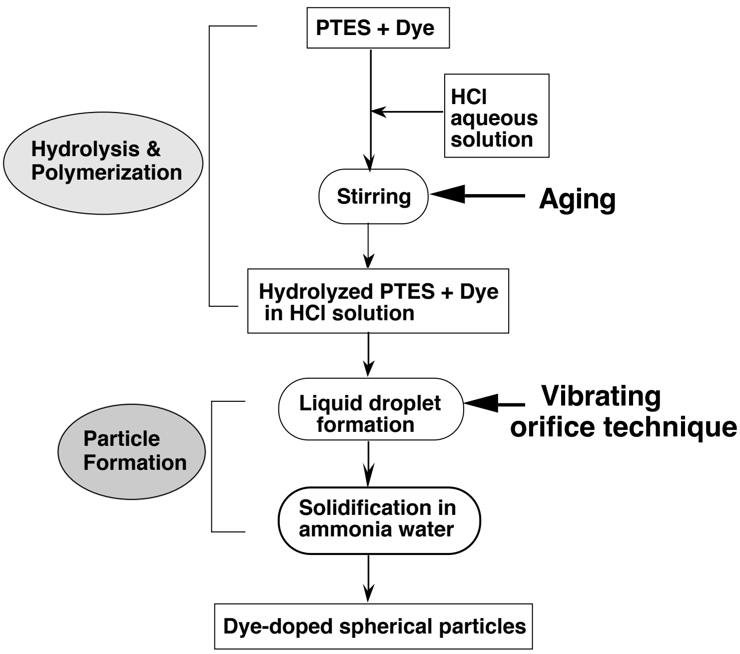

Fig. 1 Processing steps for preparing Rhodamine 6G-doped spherical particles

In the process (a), hydrochloric acid solution (pH 3) was used to hydrolyze the mixed solution of PTES and R6G. The solution was stirred for 1 ~ 2 days at 30 ˚C in a thermostat. Polymerized PTES (oligomer) was formed in the solution, and after separation into two layers oligomer and the dye were involved in the lower layer. The process (a) have been reported in our previous works in detail [12]. The solution in the lower layer was transferred and diluted by alcohol at a certain ratio, then it stored at 30˚C for long time(designated as “aging” hereafter) in a sealed cup container. The degree of polymerization during the aging time was checked by measuring FTIR spectra of films on KBr plates made from the sol at a certain aging time. Ratio of the absorption peaks due to Si-OH (3400 cm^{-1}) and phenyl group (740 cm^{-1}) was a suitable indicator of the polymerization.

In the process (b), after aging from several to several ten days, the resultant solution was supplied to a liquid droplet generator using a constant-flow syringe pump. In Fig. 2, liquid droplet formation by the vibrating orifice technique is illustrated. A cylindrical liquid jet (PTES oligomer and R6G diluted with alcohol) passing through the orifice of 10 and 20 μm in diameter breaks up into equal-sized droplets by mechanical vibration (using piezoceramics with frequency of 70 ~ 200 kHz). Alcohol solvent of these droplets was evaporated during flying with carrier gas (air) and subsequently solidified in concentrated ammonium water trap of 3 – 12 mol/l. Surface active reagents such as Polyoxyethylene sorbitain monoleate (Tween-80) and Dodecyl benzene sodium sulfonate (DBSS) was mixed with ammonia water to avoid coagulation of particles. Then the solution containing dye-doped particles was washed by pure water and used for the following optical measurements.

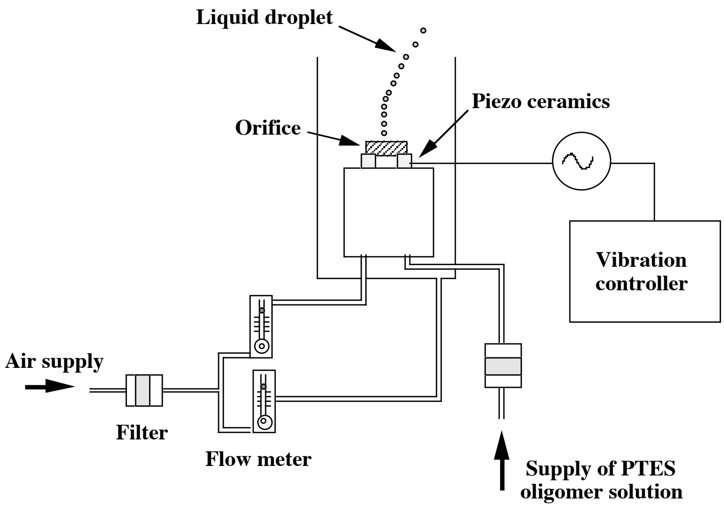

Fig. 2 Liquid droplet formation by the vibrating orifice technique.

Sizes of dye-doped particles were estimated by a scanning electron microscopy (SEM).
Illustration of set-up for the measurements of the resonance effects in spherical particles is shown in Fig. 3. Spherical particles were set on a glass plate under an optical microscope in an air and one of them was pumped by a second harmonic pulse of Q-switched Nd:YAG laser (Spectra Physics Co, GCR-16). For guiding the pumping laser light into an optical microscope and the emitted light from the particle, silica glass optical fibers were used. After eliminating the pumped laser light by a notch filter, the emitted light was detected by image-intensified CCD array with an electric gate (ICCD-576G-1, Prinston Instrument Inc.). The gate of the detector was synchronized with Nd:YAG laser through the pulse generator controlled by computer. Pulses were :wavelength of 532 nm , repetition rate of 10 Hz, and pulse duration of about 5 nsec. The diameter of the pumped spherical particle was measured in situ using the optical microscope with CCD detector.

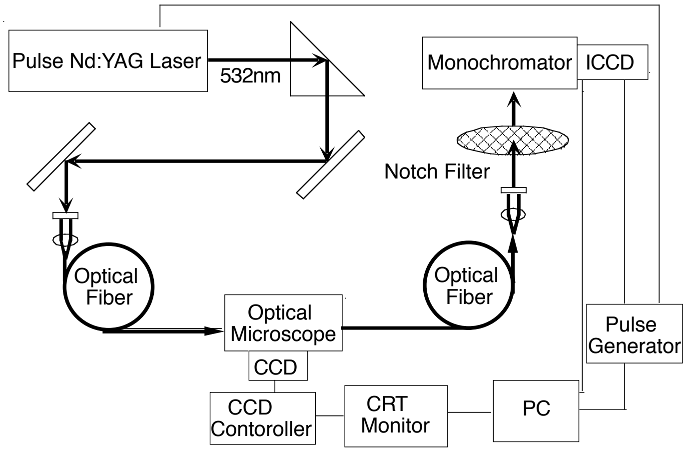

Fig. 3 Set-up for measuring the laser emission from a R6G-doped spherical particle

3. RESULTS

SEM photographs of spherical particles made from the sol of various aging time are shown in Fig. 4. Sol with suitable aging time (3 ~ 50 days at 30˚C) gave remarkable monodispersed particles, as shown in the photographs. With increasing the aging time more than 50 days, however, surface irregular particles were formed. Size of the spherical particles could be controlled within 0.1 μm by choosing the suitable preparation condition. The particle diameter is given by[13]

$$d = \left(\frac{6QC}{\pi f} \right)^{\frac{1}{3}} \ldots (1)$$

where Q is the liquid flow rate which was supplied by a syringe-type pump, C is the volumetric concentration of solute in the solution, and f (Hz) is the disturbance frequency. Thus, under the condition of the Q and f was fixed, just the C was changed by diluting the starting solution which involves PTES oligomer and R6G dye. In Fig. 5, average diameter of the particles were plotted against concentration of the solute in the starting solution. Precise control of diameter was achieved by changing the concentration of the solute.

Aging: 3 days 9 days 54 days

Fig. 4 SEM photographs of R6G-doped sperical particles made from sols of various aging time (Bar is 10 μm.).

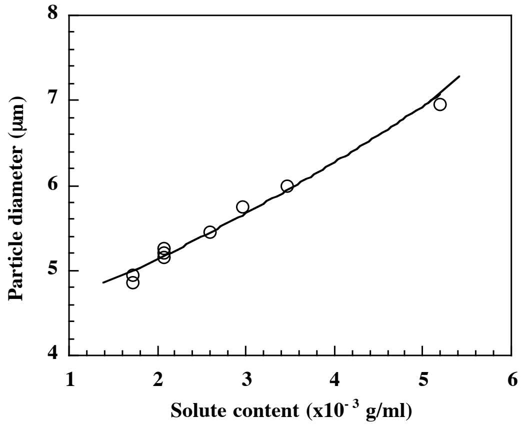

Fig. 5 Diameter of spherical particles as a function of dilution of the starting sol.
Preparation conditions are: orifice diameter = 20 μm, f = 69 kHz, Q = 8.2 X 10^{-4} cm/sec.

The emission spectra from a Rhodamine 6G-doped spherical particles (diameter: 2r = 5.6 μm and 9.4 μm) are shown in Figs. 6. Peaks in the figures correspond to the whispering-gallery mode resonance. Number of modes depended on the particle diameter: number of the peaks increased with increasing particle diameter.

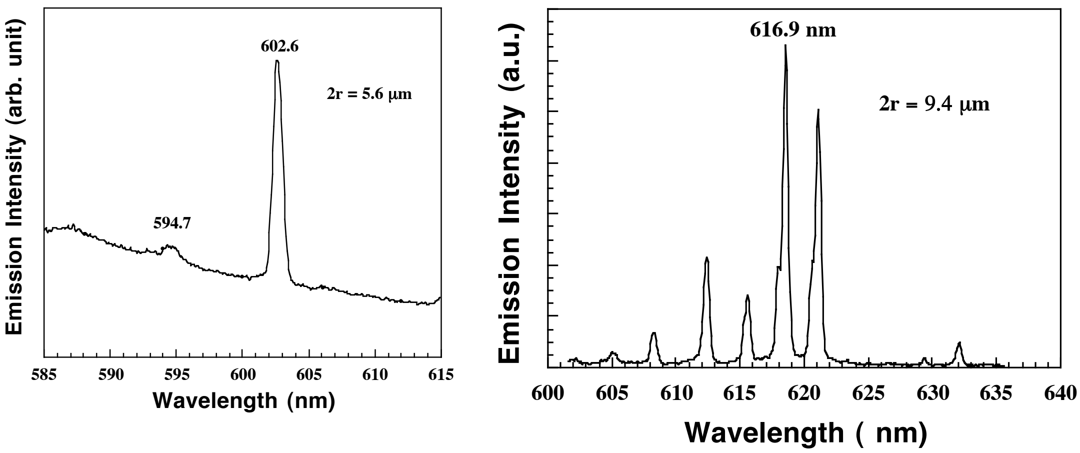

Fig. 6 Laser emission spectra for R6G-doped spherical particles of different sizes

Photodegradation of lasing emission was measured against shot number of the laser pumping at 532 nm wavelength. Typical data of degradation for the particle of 2r = 9.4 μm is shown in Fig. 7. After 2000 pulses (repetition rate of 10 Hz at 532 nm) output energy at 616.9 nm wavelength (strongest peak of the emission, see Fig. 6) was consumed 50 % of the initial value, and after 8000 pulses 90 % was consumed. Considering the detection limit of the detector, extrapolation showed that the laser emission will be observed after 15000 pulses.

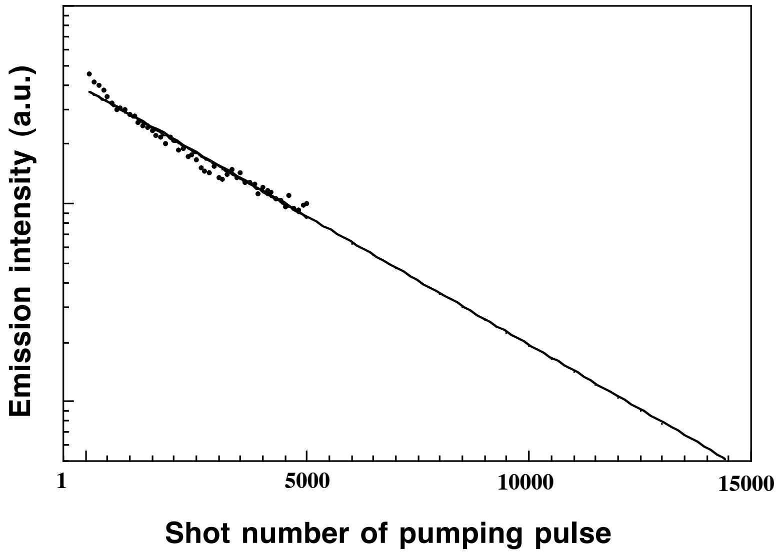

Fig. 7 Emission intensity as a function of pumping pulse number.
Diameter of the spherical particle was 9.4 μm. Peak wavelength was 616.9 nm.

4. DISCUSSION

In vibrating orifice technique, diameter of each liquid droplet can be controlled precisely. After evaporating of solvent in air gas flow and solidifying in ammonia water, monodispersed solid spherical particles were obtained. As shown in Fig. 4, the size distribution is remarkably narrow and reproducible. For solidification, ammonia water is necessary: no particle was formed and trapped in pure water. Surfactants such as Tween-80 and DBSS mixed with ammonia water showed a remarkable effect on preventing each particle from sticking. Moreover, particle sizes can be changed by choosing solute and solvent ratio as shown in Fig. 5.

Degree of the polymerization increased with increasing aging time, and after above 50 days, surface irregular particles were formed as shown in Fig. 4. The particles with rough surface cannot be used for spherical lasers. Therefore, in this technique, highly polymerized oligomer should be avoided as the starting sol. After forming liquid droplets, their solvent must evaporate and shrink to the pre-determined diameter uniformly: typically liquid droplet of 40 μm in diameter must shrink and solidify as solid spheres of 5 μm in diameter .

The demonstration of lasing from a dye-doped spherical particle is the most reliable test for estimating its characteristics for the cavity structure: size, homogeneity and circularity etc. If they could not satisfied these requirements, the lasing was impossible. Particles of the size range of 5 to 10 μm showed the emission peaks which correspond the resonance modes as shown in Fig. 6. Resonance of spherical cavity is determined by the size parameter ($x = 2\pi r/\lambda$: λ is the wavelength in the medium) and m, the refractive index of the particle relative to that of the surrounding medium. As shown in the previous report [7], R6G-doped particles showed a wide range of absorption and fluorescence in the 430-580 nm and 520 –680 nm wavelength regions, respectively. Certain wavelengths which satisfy the above-mentioned resonance condition were chosen naturally in the fluorescence wavelength region, while the fluorescence light overlapped with the absorption band (520-580 nm) is reabsorbed, thus the emission peaks are usually observed above 580 nm wavelength.

Photodegradation of laser dye incorporated in organic-inorganic hybrid bulk matrix have been investigated by many authors. Photostability of laser dye is known to be enhanced in hybrid materials, and for Rhodamine 6G the decrease in output was measured as a function of the number of pulses. Reported data which showed good photostability were not consistent in the hybrid materials and experimental conditions, thus they gave different results: (a) output of 50 % consumed after 3000 pulses and 90 % consumed after 9600 pulses (10 Hz with 3 mJ/pulse at 532 nm)[14], (b) 50 % consumed after 750 pulses (1 Hz at 337 nm) [15], (c) 50 % consumed after 1000 pulses (1 Hz with 0.7 mJ/pulse at 532 nm) [16]. Although the precise comparison among them is difficult, roughly speaking the present photodegradation in spherical cavity structure of Rhodamine 6G/ PTES oligomer seems to be comparative with the previous data. Choosing appropriate matrix and dyes (covalently bonded dyes are also suitable) will lead to improvements in laser life time of spherical particles.

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