Sol–Gel-Derived Spheres for Spherical Microcavity

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ABSTRACT
Encapsulation of light to small spheres ensures the highest quality factor (Q factor) to enhance the interaction between light and materials. In this Account, we describe the fabrication of micrometer-sized spherical particles of organic–inorganic hybrid materials to study the potential ability as a spherical cavity laser. The spherical particles prepared by the vibrating orifice technique included those of nondoped and doped with organic dyes and rare-earth-metal ions, and some of them were cladded with low-index-coating hybrid materials. Coating of the spheres was carried out by aiming at practical applications: high refractive index spheres from n_D = 1.72 to 2.5 prepared by the technique and glass spheres of n_D = 1.93. They were pumped by second harmonic pulses of a Q-switched Nd:YAG laser (532 nm wavelength) and CW Ar^+ laser (514 nm wavelength) to investigate as spherical cavity microlasers. The emission from spheres originated from the photoluminescence of dopants and Raman scattering of matrix materials. Lasing or resonant light emission from these spheres were performed by the direct-laser-light-pumping and the light-coupling techniques using an optical waveguide coupler.

1. Introduction

Encapsulation of light in the cavity structures has been an essential requirement for small-sized optical devices. Conventional optical fibers, fiber lasers, and semiconductor lasers are successful examples of the light encapsulation in one- and two-dimensional cavities. Recently, there has been a considerable interest in a spherical cavity of micrometer size: light encapsulation in three-dimensional cavity. Spherical particles are expected to have potential uses, such as a light source of multiwavelengths,[1] component of photonic crystals,[2] a low-threshold laser,[3] and so on. In Figure 1, a lasing action from a sphere is illustrated. In a sphere, activated light by a laser pumping forms whispering gallery modes (WGMs) by total internal reflection along the curved boundary between the sphere (refractive index n_1) and the surrounding medium (index n_2). Quality factor Q of WGM depends upon the diameter and relative refractive index $n_r = n_1/n_2$ of the sphere. High n_r is inevitable to accomplish the spherical optical cavity structure in micrometer-sized spheres. WGM enables us to perform a strong interaction between laser light and materials and results in superior effects in a small volume. Using the WGM resonance, lasing can be achieved at a much lower excitation intensity than within the corresponding bulk materials,[4] and recently, spherical cavity-based Raman lasers were performed with ultrahigh-Q silica microspheres using fiber-taper couplers.[5]

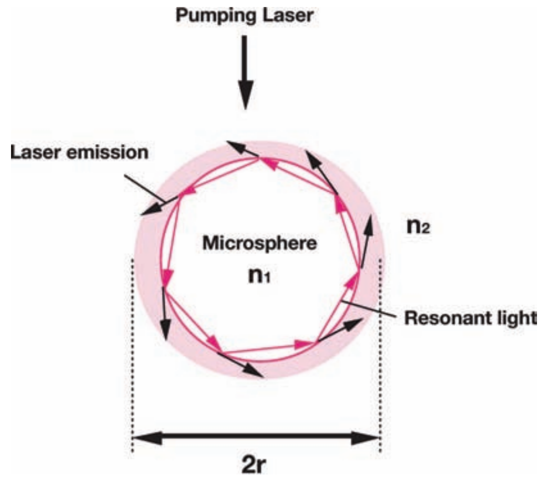

FIGURE 1. Schematic illustration of the excitation of WGMs in a dye-doped microsphere. In a sphere, fluorescence light excited by a laser pumping forms WGMs by total internal reflection along the boundary between the sphere (refractive index n_1) and the surrounding medium (index n_2).

A brief history of spherical cavity research, especially lasing demonstration, is presented in Figure 2. The first spherical laser was reported in a Sm^{2+} in a CaF_2 sphere of millimeter size in 1961.[6] It is well-known that the Fabry–Perot-type conventional lasers have been developed rapidly and enormously. In the field of spherical lasers, however, fundamental research continued for a long time because of the difficulties in fabricating micrometer-size spheres and controlling the laser actions. The previous investigations are classified into two groups: (1) from liquid droplet to dye-doped spheres where the sizes of spheres progressively decreased for years and (2) high-quality factor (high-Q) solid spheres of relatively large sizes, along with the improvement in coupling efficiency of pumping laser light into spheres.

In the first research flow, in 1984, lasing from dye-dissolved ethanol droplets in 60 μm diameter was re-

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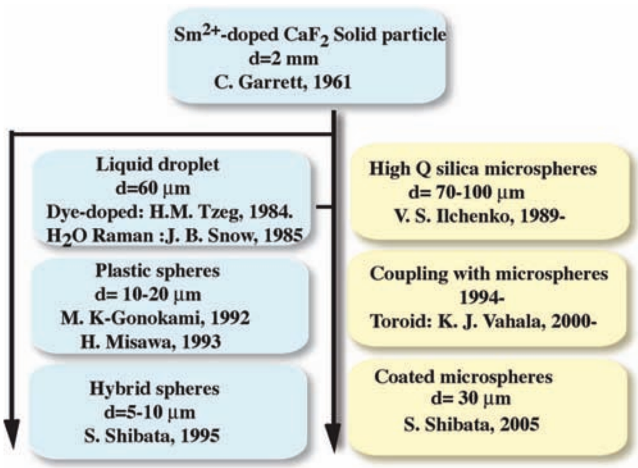

FIGURE 2. Brief research history of spherical mivrocavity, especially lasing demonstration.

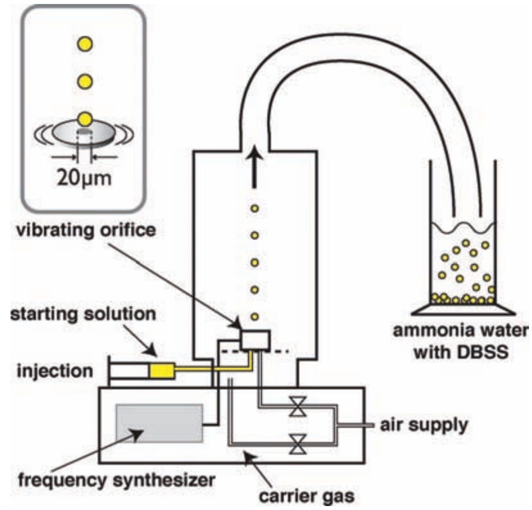

FIGURE 3. Fabrication of spherical particles by the vibrating orifice technique.

ported,[7] which is the revival of the spherical-laser research. After the report, lasing from various dye-doped spherical particles have been demonstrated by many authors: plastic particles of ~10–20 μm in diameters[8,9] and organic–inorganic hybrid particles of 6 μm in diameter.[10,11] We have reported lasing from dye-doped hybrid spherical particles made by the "vibrating orifice technique", which gave us size-controlled particles within ±1% accuracy in diameter.[12] Using these dye-doped particles, we can choose suitable dye content and low pumping power, and the photostability under laser action was improved remarkably.[13] From a practical point of view, for preventing surface contamination and maintaining the ability of optical performances, the microspheres should be coated with clad materials of lower refractive index than those of spheres. Thus, to meet the requirement of the high relative refractive index n_r ($n_r > 1.5$) as a spherical cavity, high index spheres $n_{core} > 2.0$ are needed.[14]

In the second flow, much attention has been directed at investigating optical resonances (WGM) of glass microspheres.[15] Long confinement time (high-Q for high-purity silica glass spheres: $Q = 10^{10}$) achieves a strong interaction of light and materials with enormous photostability.[16,17] To excite high-Q microspheres, we need to couple laser light into them effectively. Various techniques for achieving sufficient coupling have been tried using prism couplers, fiber tapers, side-polished fibers, hybrid fiber-prism couplers, slab waveguides, and so on.[18,19] Recently, Silica-glass microspheres and microtroids pumped by fibers taper have been demonstrated as superior resonators of high-quality factor and high optical performances.[20]

Microcavity-based Raman lasers are highly attractive for extending the wavelength range of the existing laser sources. Early works showed that the stimulated Raman scattering is possible in water droplets of 60 μm in diameter.[21,22] Recently, a Raman laser was performed with ultrahigh-Q silica microspheres (40–70 μm in diameter) using fiber-taper couplers.[5] The fiber taper is efficient for optical coupling, but it requires delicately drawn fiber of a few micrometers in diameter suspended in air. Moreover, the refractive index of high-purity silica glass is as low as 1.458. A lower index than that for the cladding is not readily available. Therefore, we recognize the urgent issues for high-Q microspheres as (a) high refractive index spheres, (b) coating of spheres, and (c) efficient coupling to spheres for meeting the requirement in practical devices.

We describe three topics in our laboratories using organic–inorganic hybrid materials: (1) lasing from dye-doped spherical particles ($n_D = 1.5$) and the improvement in photostability, (2) fabrication of high refractive index ($n_D > 2.0$) spheres and measurement of optical properties of Eu ion-doped spheres, and (3) coating and pumping by laser coupling of the coated high-index spheres.

2. Fabrication of Spheres

Spherical particles were prepared by the vibrating orifice technique as illustrated in Figure 3.[12] Starting reagents phenyltriethoxysilane (PTES) and diphenyldimethoxysilane (DPhDMS) were hydrolyzed and polymerized in hydrochloric acid solution. For high-index particles, titanium tetra-*n*-butoxide (TTBu) was added at 3 °C for controlling its high reactivity.[14] Laser dyes, such as rhodamine 6G (R6G) and 4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4H-pyran (DCM), were added to the starting sol. In the fabrication of doped spheres, the good affinity between the dopant and the materials of the sphere is always very important. For example, phenyl groups connecting in the matrix network are inevitable to incorporate organic dyes in the sphere,[23] because the hydrophobic–hydrophilic relation between the matrix and dopant materials decides the affinity. For Eu ion doping, europium(III) thenoyltrifuoroacetonate [Eu(TTFA)$_3$] was chosen as a doping reagent, which is easily dissolved in an ethanol solvent and uniformly incorporated in the sphere matrix. If inorganic salts of Eu were adopted, undesirable coagulation occurred because of the mismatching of dopants and the hybrid matrix. The starting solution diluted with alcohol was supplied to the liquid

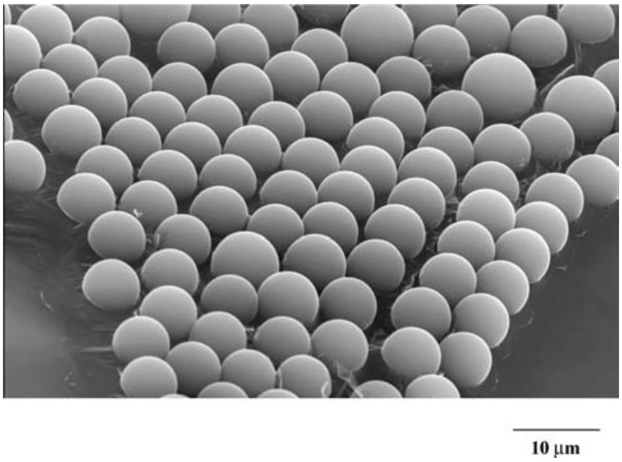

FIGURE 4. SEM photograph of spherical particles made by the vibrating orifice technique.

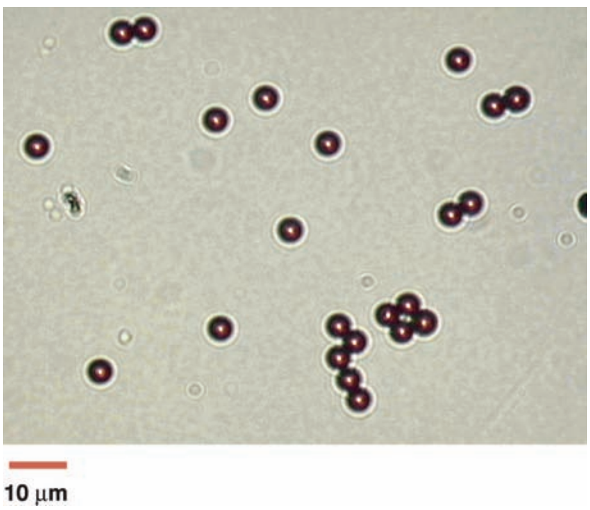

FIGURE 5. Photographs of dye-doped microspheres by an optical microscope.

droplet generator using a constant-flow syringe pump. A cylindrical liquid jet of diluted hybrid raw materials dissolving the dopants passing through an orifice (20 μm in diameter) breaks up into equal-sized droplets by mechanical vibration. Then, the solvent was evaporated during flying with carrier gas, and subsequently, these droplets solidified into hybrid microspheres in ammonium water. Dodecyl benzene sodium sulfate (DBSS) was added into the trapping container to avoid coagulation of particles. By choosing the following parameters, we can control the sizes of the sphere precisely in the range of 4–10 μm, solute concentration in the starting solution, feeding speed into the orifice, and the frequency of the orifice vibration.[12,24] The scanning electron microscopy (SEM) photograph of spherical particles and those observed by an optical microscopy are shown in Figures 4 and 5. Narrow size distribution is remarkable, and the dye-doping efficiency is nearly 100% in the content of $\sim 10^{-7}$–10^{-4} mol/g.

The hybrid optical waveguide was fabricated on a silica glass substrate using sol–gel lithography techniques. 3-Methacryloxypropyl-trimethoxysisilane (MOPS) was hydrolyzed in hydrochloric acid solution; then tetramethoxyorthosilicate (TMOS) was added; and finally titanium tetraisopropoxide (TTIP) was titrated into the sol. Photoinitiator of IRGACURE 184 (CIBA) was added into the resultant sol, and films of 10–15 μm in thickness were prepared by the dip-coating technique under a dry N_2 gas atmosphere. Because the sol–gel hybrid films are sensitive to moisture in air, a dry gas atmosphere is inevitable to avoid the formation of cellular patterns in sol–gel coating process.[25] Suitable conditions should be chosen to carry out the precise photolithography, especially prebaking condition, UV power, and content of photoinitiator.[26] The films were prebaked and exposed UV irradiation through a fused silica chromium photomask. Samples were then soaked in 2-propanol to remove the unexposed area, followed by the postbaking.

Commercially available high-index glass spheres of 30 μm in diameter, made by the flame spray technique, were used for the coating experiments. The composition of the glass spheres was BaO–SiO_2–TiO_2, and their refractive index and specific gravity are 1.93 and 4.1 g/cm^3, respectively. In the flame spray technique, where small pieces of glass cullet were melted in the flame, glass spheres with a smooth surface were formed by the surface tension. The smooth surface by the melting process is essential to the high-Q spherical cavity. Coating material was silicone oligomer (GR100), having methyl and phenyl groups of a 2:1 molar ratio, with a refractive index of 1.49 and specific gravity of 1.3 after curing. The silicone oligomer was diluted with an acetone solvent, and the alkali reagents were added to accelerate the polymerization. The glass spheres dispersed in a GR100–acetone solution were sprayed with air-spray equipment on a Teflon sheet substrate. Coated spheres were dried at room temperature followed by heating up to 130 °C. Sol–gel-derived high-index spheres of 80TTBu-20DPhDMS (after heating at 550 °C) were also coated using GR100 solution. Typical properties of coated high-index spheres are refractive index $n = 2.5$ for the core and 1.49 for the cladding ($n_{relative} = 1.7$), core diameter of 5 μm, and outer diameter of about 15 μm. Coating thickness was influenced by the affinity between the core and clad materials and the solute concentration in the solvents.

SEM photographs of the coated-glass spheres prepared from the starting sols containing the GR100 reagent of 5 and 40 mass % are shown in parts a and b of Figure 6. As shown in Figure 6a, below 20 mass %, glass spheres were coated uniformly. Up to 40 mass %, as shown in Figure 6b, coated glass spheres having one flat side were obtained. Because the attached side to the Teflon sheet surface shows the flat portion similar to a terrace, we called it the "terrace microsphere" from their impressive shapes.

3. Optical Characteristics of Spherical Particles

3.1. Laser Emission from Dye-Doped Spherical Particles. Because the matrix of the spheres was chosen to have good affinity with organic dyes, the incorporated

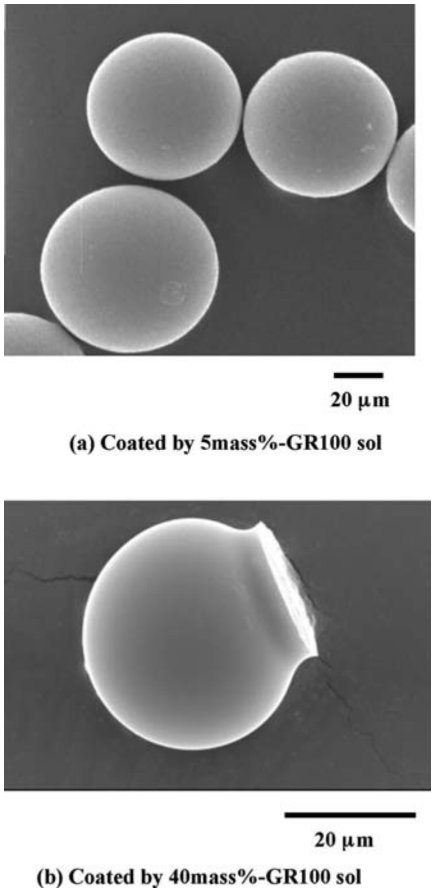

FIGURE 6. SEM photographs of the coated glass spheres prepared from the starting sols containing a GR100 silicone oligomer of (a) 5 mass % and (b) 40 mass %.

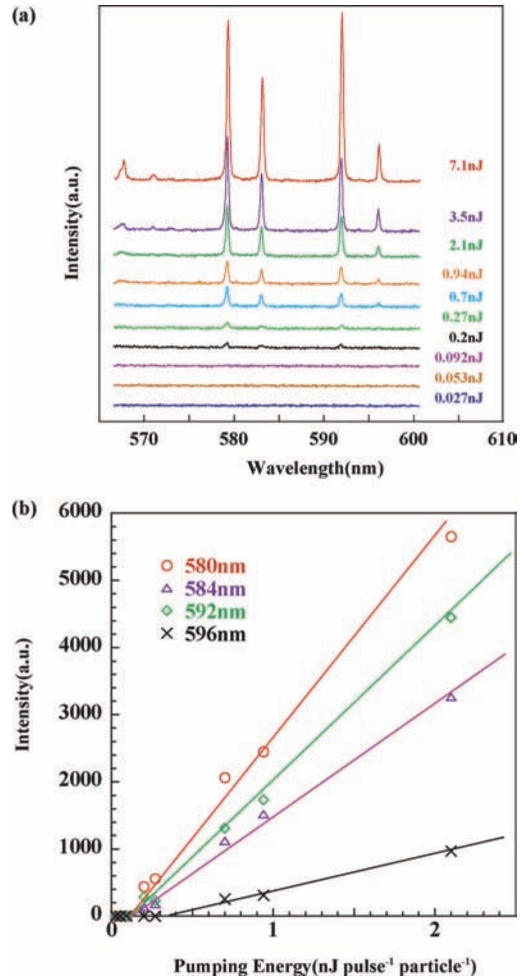

FIGURE 7. Typical example of an emission spectrum from a R6G-doped sphere (a) and the emission intensity as a function of the pumping power (b). The diameter of the sphere was 6.2 μm, and the R6G content was 1×10^{-6} mol/g.

dyes showed only a monomer-like absorption spectrum, which is similar to that dissolved in ethanol (known as the good solvent for the laser dyes). Spherical particles were set on a glass plate under an optical microscope in air, and one of them was pumped by a second harmonic pulse of a Q-switched Nd:YAG laser.[13] Pulses were at 532 nm wavelength, 10 Hz repetition rate, and 5 ns duration time. A notch filter eliminated the pumped laser light, and then the emission was measured by an image-intensified charge-coupled device (CCD) array with an electric gate. Photodegradation of the laser emission from various dye-doped spherical particles was measured by pulse pumping up to 100 000 shot numbers.

A typical example of the emission spectrum from a R6G-doped sphere and the emission intensity as a function of the pumping power are shown in Figure 7. The wavelength region of the emission was ~570–600 nm. Peaks in the figure corresponded to WGMs, and the number of modes depended upon the particle diameter. The wavelength region of the emission peaks was determined spontaneously by incorporated dye species and its content, because the overlap region of the absorption and the fluorescence bands did not show the laser emission, and thus, the emission was observed at longer wavelengths than the overlap region.

With an increase of the R6G content, a rapid decrease of emission intensity was observed. On the other hand, the threshold intensity decreased with an increasing dye content, which means that we can decrease the pumping power. Because the most stable lasing conditions are obtained by choosing the lower dye content and the lower pumping power, we should determine the cross-point conditions for achieving high-degradation-resistant dye-doped spheres from these contradictory results. In Figure 8, the typical example of photodegradation of DCM-doped spheres is shown. By extrapolation, we know that after 260 000 shot irradiation the emission consumes 50% of the initial intensity. Because the lifetime (50% consumption of the initial intensity) of laser emission in dye-doped hybrid bulk materials is several thousand pulses,[27,28] the result in Figure 8 is remarkable.

In parts a and b of Figure 9, the photographs of a spherical particle pumped by an optical waveguide are shown. Figure 9a showed a photograph of a sphere just placed with a waveguide (not pumping). CW Ar^+ laser light (514.5 nm) was introduced into an optical waveguide, and evanescent coupling light pumped a dye-doped sphere placed in contact with an optical waveguide. When the pumping light was removed using an edge filter, emitted

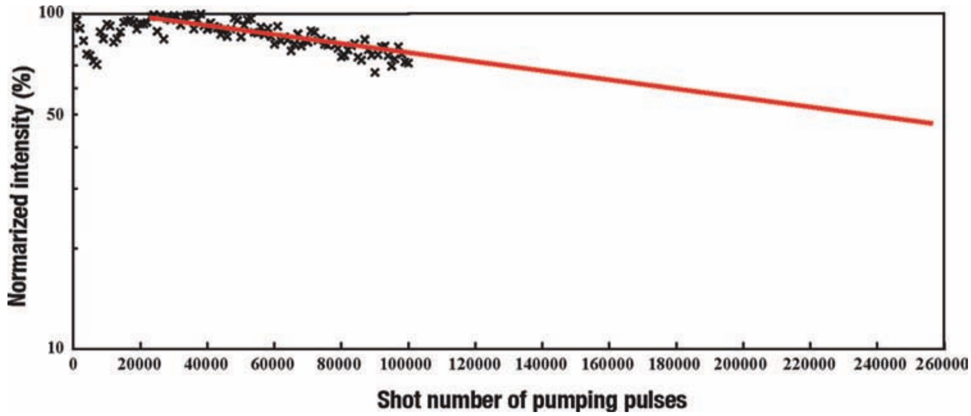

FIGURE 8. Typical example of photodegradation for the sample under the most suitable conditions (DCM-doped particles; pumping, 0.7 nJ particle^{-1} pulse^{-1}).

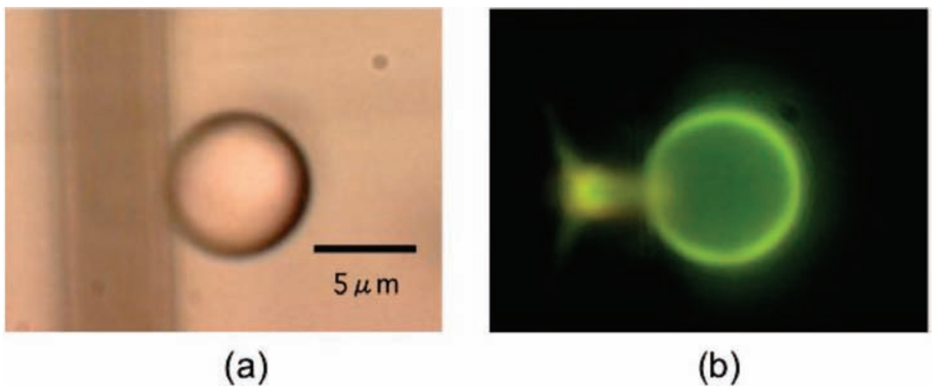

FIGURE 9. Photographs of a spherical particle pumped through a waveguide, which was made from sol–gel hybrid materials by photolithography. (a) Sphere placed with a waveguide. The waveguide width is 4 μm, and the diameter sphere is 7.2 μm, with R6G content of 1×10^{-6} mol/g). (b) Sphere pumped by CW Ar^+ laser light (514.5 nm) through the optical waveguide (pumping light of 514.5 nm was cut by an edge filter).

light was clearly detected by the CCD array. Ring-shaped bright light was observed at the surface of the spherical particle (see Figure 9b), which confirmed the optical resonance effect of the dye-doped sphere.[26] The emission spectrum showed the resonance peaks corresponding to WGMs.

3.2. Emission from Coated Spheres.

3.2.1. High-Index Sol–Gel-Derived Spheres: Eu Ion-Doped Spheres. The change in the refractive index of 80TTBu-20DPhDMS samples is plotted in Figure 10 after heating at various temperatures. The index was estimated by two different techniques: (a) the optical interference method for thin films prepared from the same starting sol as the spheres (●)[24] and (b) the mode spacing of the resonant emission from Eu-ion-doped spheres (○). The refractive index increased with an increasing heating temperature, and $n_D = 2.6$ was attained after heating at 550 °C. Such high-index values are attributed to the high content of the TiO_2 component in the sphere. With an increasing temperature, the diameter of the spheres was decreased: typically, from 5.2 μm at room temperature to 3.8 μm after 550 °C of heating. In the heating process, the solvent evolved completely and the organic groups in the hybrid spheres decomposed. A high content of TiO_2 increased the resultant refractive index. Such a high index is not surprising, because TiO_2 is known to be as high as $n_D = 2.6$–2.9 in the rutile form.[29]

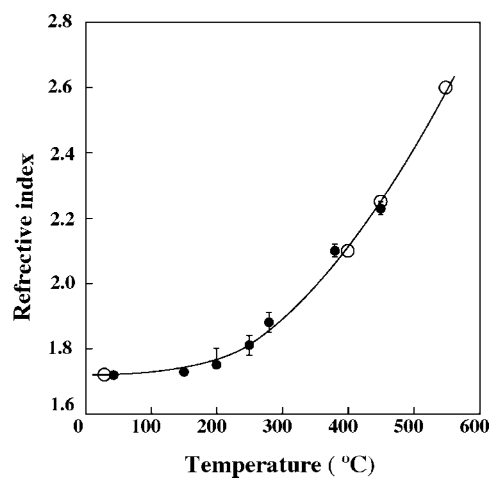

FIGURE 10. Change in refractive index of high-index hybrid spheres after heating at various temperatures. A typical composition of the high-index spheres was 80TTBu-20DPhDMS. Indices were estimated by the optical interference method (●) and the mode-spacing method for the resonant emission from Eu-ion-doped microspheres (○).

Emission spectra from Eu-ion-doped high-index spheres after heating at 400 and 550 °C are shown in Figure 11.[24] A periodic sharp ripple attributed to MDRs was observed in the spheres heated up to 400 °C. The bands at 200–1000 and 2000–4000 cm^{-1} originated from Raman scattering of titania–silica matrix[30] and the fluorescence of $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions of Eu^{3+},[31] respectively. A

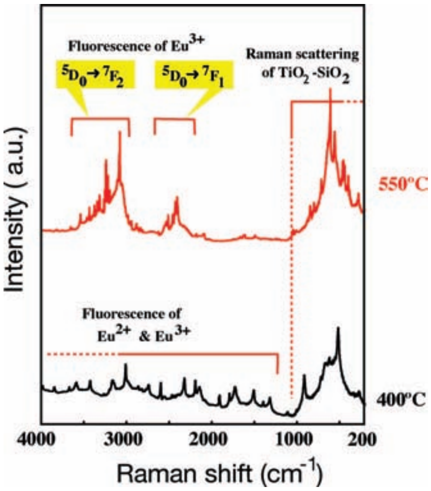

FIGURE 11. Emission spectra from Eu-ion-doped high-index spheres after heating at 400 and 550 °C. Excitation was carried out using a CW Ar^+ laser (514.5 nm wavelength and 35 mW power).

plausible explanation for the difference between the spectra at 400 and 550 °C is the coexistance of Eu^{2+} and Eu^{3+} in the 400 °C sample. Organic groups, such as phenyl in the starting spheres (confirmed from the Raman bands of phenyl groups of 600, 1000, and 1600 cm^{-1}), disappeared above 250 °C; thus, evolution of carbon induced the reduction of the Eu ion. It is also noteworthy that both of the Raman and fluorescence bands are observed in the same spectra of high-index spheres under the resonant condition.

3.2.2. Coated High-Index Spheres. From a practical requirement for preventing surface contamination, microspheres should be coated with low-index clad materials. To achieve laser emission from the spherical cavity, a high refractive index difference ($n_{relative} > 1.5$) between the microspheres and surrounding medium is inevitable. In the previous papers,[1,5,10] the pumping experiments were generally carried out in air to meet the requirement of the high-index difference. We have perceived that high-index microspheres (high-TTBu-content hybrid spheres of $n_D > 2.0$) were fabricated by the vibrating orifice technique, with subsequent heating.[14] High-index Eu-doped spheres (after heating at 550 °C) were coated with a silicone oligomer (GR100) and excited with an Ar^+ laser. Typical sizes of the core and the outer diameter are 3.8 and 5.1 μm, respectively, and the relative refractive index n_r ($n_r = n_{core}/n_{clad}$) was 1.74. A similar emission spectrum as those in Figure 11 with the WGM-mode ripples was obtained.[32] The WGM resonant emission was also confirmed from the coated Eu^{3+}-doped high-index spheres.

Another experiment was carried out for coated high-index glass spheres. Raman emission spectra of the "terrace microsphere" with various irradiation points are shown in Figure 12.[33] The corresponding laser pumping spots (from A to E) are illustrated at the right side of the figure. The various points on the sphere were irradiated and excited by the laser, and the changes in emission spectra were studied. When the terrace point (spot B) was pumped, the coated sphere showed the remarkable increase of the emission intensity, as shown in the figure. On the other hand, at the opposite point E (the uniformly coated area), we cannot observe the resonant emission. Above the threshold input power at about 4 mW, the stimulated Raman emission from terrace microspheres showed lasing action. To achieve the resonant condition inside the sphere, the excitation at the tangent line is suitable, but under the perfect spherical condition, the light cannot penetrate into the sphere and almost all of the energy will be reflected. The contradictory conditions: lowering the reflection at the surface and matching the angle for the resonant condition seem to be satisfied by the terrace structure.[33] Although commercially available glass spheres were used in the experiments, we now developed a new fabrication technique to prepare super-

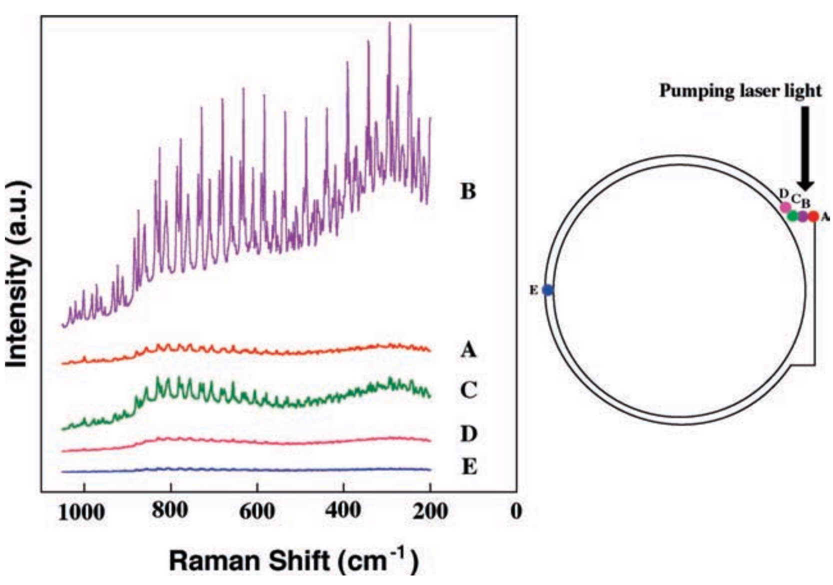

FIGURE 12. Raman emission spectra of the "terrace microsphere" with various irradiation points. Glass spheres have a refractive index $n_D = 1.93$ and 30 μm in diameter. The corresponding Ar^+ laser pumping spots (from A to E) are illustrated on the right side of the figure. The pumping laser intensity was 10 mW, and the spot size was 1 μm in diameter.

spherical glass and confirmed the WGM resonant emission as an optical resonator.[34,35]

4. Concluding Remarks

Among various cavity structures, a spherical cavity of several ten micrometers in size shows the highest Q value ($Q = 10^{10}$ of WGM in silica glass microspheres).[17,20] Therefore, we recognize that transparent spheres have the ability to confine laser light within the small volumes to enhance the enormous interaction between light and materials, which leads to low-threshold lasers and optical small devices using nonlinear optical effects, such as stimulated Raman scattering. The fiber-taper coupling is known to be the noble and elaborate technique in laboratory-scale experiments to investigate optical encapsulation studies. Unfortunately, however, it could be difficult for commercial applications, because of the poor mechanical strength of the taper-shaped portion and the contamination problem caused by the setup suspending in air. Thus, the urgent issues for commercial use of high-Q microspheres are the fabrication of high refractive index spheres, coating, and efficient optical coupling of laser light for meeting the requirement in practical devices.

We started the investigation from the development in fabricating microspheres of hybrid materials, because we have accumulated the knowledge in sol–gel technology to make spheres, and the vibrating orifice technique (used in "an ink-jet printer") for preparing equal-sized hybrid spheres. Dye-doped microspheres are highly efficient for photoluminescence; thus, they have been tried in the early stage of our investigation. Dye-doped particles of 4–10 μm were prepared, and the improvement of the lifetime of doped dyes was demonstrated. Pumping dye-doped spheres through an optical waveguide was one of the successful results. They could be useful in the biology research area as high-sensitive probes.

At the second stage, we have tried to develop high refractive index spheres >2.0 for preparing the coated spheres by low-index cladding to adapt them to stable optical performances. Moreover, another demand to the spheres is the development of a new optical coupling technique available for such high-index spheres. The terrace microspheres to several ten micrometers in diameter are one of the elaborate optical coupling techniques, which also satisfy the coating requirement. From the practical viewpoints, the terrace structures are remarkable because they are applicable to the integrated circuits using the planar waveguide technology.[33] The terrace microspheres also have potential to be used as filters, light sources, and optical switches. The combination of high-index spheres by the sol–gel technique and the terrace microspheres will be the answer to open a new way for commercial optical-cavity devices.

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