論文 / 著書情報
Article / Book Information

論題(和文)	
Title(English)	Hybrid Microspheres for Optical Application
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出典(和文)	, Vol. , No. , pp. I-11-020
Citation(English)	XX International Congress on Glass, Kyoto, Japan, Vol. , No. , pp. I-11-020
発行日 / Pub. date	2004,

HYBRID MICROSPHERES FOR THE OPTICAL APPLICATIONS

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Micrometer-sized spherical particles of organic-inorganic hybrid materials were fabricated by the vibrating orifice technique for the wide variety of optical applications. A cylindrical liquid jet of diluted hybrid raw materials passing through an orifice 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. Various microspheres were prepared by this technique: those of non-doped or doped with organic dyes, rare earth ions and Ti alkoxide. Their refractive indices were n_D=1.48-1.72 at room temperature. They were pumped by second harmonic pulses of Q-switched Nd:YAG laser (532nm wavelength) or CW Ar^+ laser (514nm wavelength) to investigate as spherical cavity micro-lasers. Lasing or resonant light emission due to photoluminescence were performed by direct laser light pumping and light coupling from waveguide to microspheres. Emission peaks corresponded to the spherical resonance modes of the microsphere and the number of mode and the mode spacing depended on the refractive index and the particle diameter. Optical applications and technological use of these hybrid microspheres will be discussed in the presentation.

(Key words: sol-gel, hybrid microsphere, spherical cavity laser, vibrating orifice technique)

1. Introduction

Encapsulation of light in the cavity structure has been a stimulated interest for small-sized optical devices. Conventional semiconductor lasers and optical fibers are successful examples of the light encapsulation in one and two dimensions. Recently there has been a considerable interest in a spherical cavity of micrometer size: Light encapsulation in three dimensions. Spherical particles of cavity structure are expected to have potential uses such as a light source of multi-wavelengths, probes for near-field scanning optical microscopy [1], components of photonic crystals [2], a low-threshold laser [3] and so on. Optical resonance in microspheres (whispering gallery modes, WGM) enables us to achieve a strong interaction between laser light and materials, and results in a superior effect in the small devices. Using the WGM resonance, for example, lasing can be achieved at much lower excitation intensity than within the corresponding bulk materials [3].

The first spherical laser was reported in an Sm^{2+} in CaF_2 sphere of millimeter size in 1961[4]. The Fabry-Perot type conventional lasers have been developed rapidly and enormously. In spherical lasers, however, fundamental researches continued for a long time because of the difficulties in fabricating and controlling the laser actions. In 1984, lasing from dye-dissolved ethanol droplets in 60μm diameter was reported [5], which is the revival of the spherical lasers. After the report, lasing from various dye-doped spherical particles have been demonstrated by many authors: plastic particles of 10~20μm in diameters [6], [7], organic-inorganic hybrid particles of 6μm in diameter [8], [9].

We have reported the noble technique for fabricating hybrid spherical particles: the vibrating orifice technique [10]. It is enables us to prepare micrometer-size spherical cavity, with high-controllable size, nearly 100% dye-doping, nanoparticle-doping and high refractive index etc. Thus using this technique, the author describes two topics in my laboratories: (1) lasing from dye-doped spherical particles and the improvement in their lifetime, and (2) pumping the spherical particle by an optical waveguide (we also fabricated the waveguide of hybrid materials by photolithography techniques).

In the near future, hybrid microspheres will be used in an optical circuit, as illustrated in Fig. 1, and open the way to new optical micro-devices such as optical sources, amplifiers, filters and so on. The paper describes the initial stage of the microspheres for various applications.

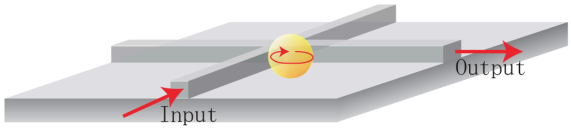


Fig. 1 illustration for pumping a microsphere by an optical waveguide.

2. Experimental

Spherical particles were prepared by the vibrating orifice technique as previously reported [9]. The technique is illustrated in Fig. 2. The starting reagents Phenyltriethoxysilane (PTES) and Diphenyldimethoxysilane (DPhDMS) (was hydrolyzed and polymerized in hydrochloric acid solution (pH 2-3) for 1-3 days at 20-30ºC. For high-index particles, titanium tetra-n-butoxide (TTBu) was added at 3ºC and for dye-doped particles laser dyes such as Rhodamine 6G (R6G) and 4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran (DCM) were added at room temperature. The process was reported previously in detail [10], [11]. Then the solution diluted with alcohol was supplied to the liquid droplet generator using a constant-flow syringe pump. A cylindrical liquid jet passing through the orifice of 20 μm in diameter broke up into equal-sized.
droplets by mechanical vibration. The droplets were carried by an air through a pipe and during the process alcohol solvent was evaporated. Subsequently these droplets were trapped and solidified in ammonium water. The solution for trapping contained Dodecyl benzene sodium sulfate (DBSS) to avoid coagulation of particles. The spherical particles were washed by pure water and stored in a container with water for the following experiments

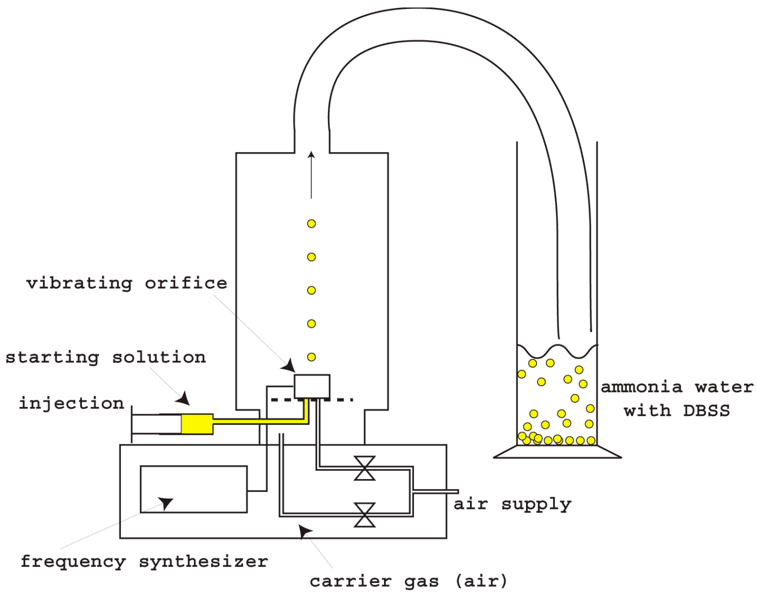


Fig. 2 Schematic illustration for the fabrication of hybrid microspheres

The hybrid optical waveguide was fabricated as follows. 3-methacryloxypropyl-trimethoxysisilane (MOPS) was hydrolyzed in hydrochloric acid solution (pH 2) and 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 10-15μm in thickness were prepared on silica glass substrates by dip-coating technique under dry N_2 gas atmosphere. The films were pre-baked at 60ºC for 50 min and were exposed UV irradiation for 20 sec through a fused silica chromium photomask. Samples were then soaked in 2-

propanol to remove the unexposed area. Post bake of the samples at 100ºC for 60 min was carried out.

The set up for measuring the emission spectrum from spherical particles is shown in Fig. 3. The 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-130) [9]. Pulses were: 532 nm wavelength, 10 Hz repetition rate and 5 nsec duration time. The dye-doped spherical particle was pumped at room temperature by the pulses transmitting through silica glass optical fibers and its emission was also transmitted another silica glass fiber to the detector. A notch filter eliminated the pumped laser light, and then the emission was measured by image-intensified CCD array (Princeton Inst., ICCD-MAX) with an electric gate. The intensity of the pumping laser light was controlled by various ND filters and measured by a power meter (J3-02, Molectron). Photodegradation of the laser emission from various dye-doped spherical particles was measured by pulse pumping up to 100,000 shot numbers.

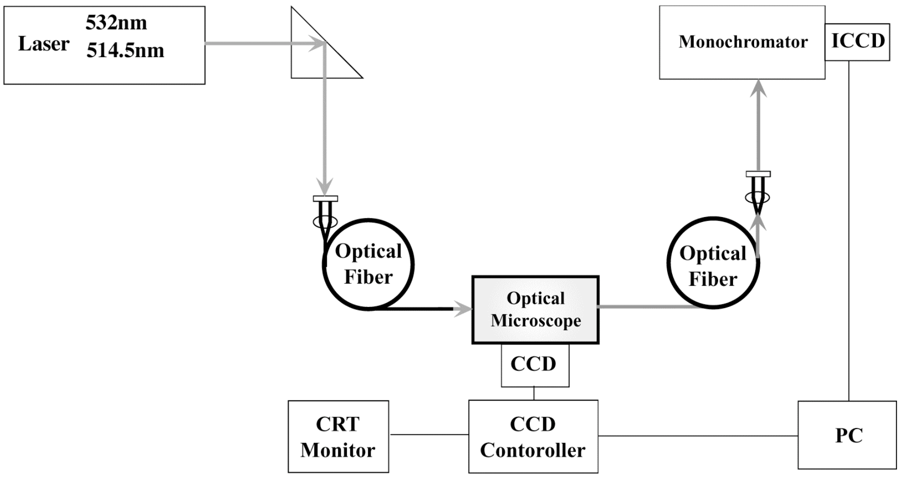
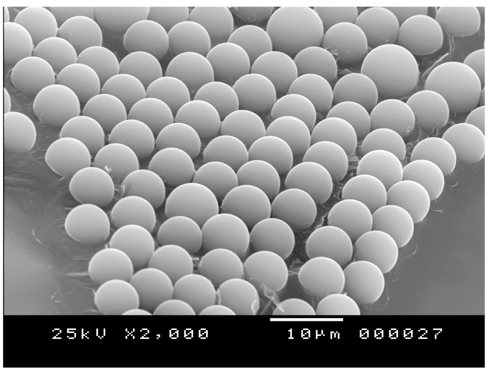


Fig. 3 Set-up for measuring the emission spectra from spherical particles.

CW Ar+ laser light (514.5nm) (Coherent Innova 70-A-2) was introduced into an optical waveguide by using a single-mode optical fiber. A spherical particle placed in contact with an optical waveguide was pumped by its evanescent light. After removing the pumping light by an edge filter, emitted light was detected by the CCD array.

2. Results

SEM photograph of spherical particles made by the vibrating orifice technique and their photograph by an optical microscopy are shown in Figs. 4 and 5. Narrow size distribution is remarkable, and the dye-doping efficiency is nearly 100% in the content of $10^{-7} \sim 10^{-4}$ mol/g.



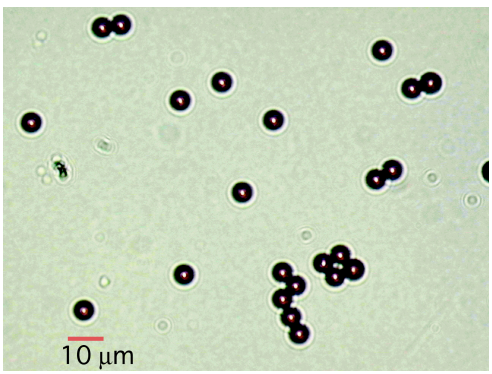


Fig. 4 SEM photograph of microspheres.

Fig. 5 Photograph of dye-doped microspheres.

Laser emission from dye-doped spherical particles

Typical example of emission spectrum from a R6G-doped sphere (upper figure) and the emission intensity as a function of the pumping power (lower figure) are shown in Fig. 6. Diameter of the sphere was 6.2 μm and the R6G content was 1X10^{-6} mol/g. The wavelength region of the emission was 570~600nm. Threshold pumping power was 0.1~0.2 nJ pulse^{-1} particle^{-1}. Peak in the figure corresponded to the whispering gallery modes, and the number of modes depended on the particle diameter. In the experiment, R6G-doped spheres of various diameters (4~12μm) were prepared and the linear relation of mode spacing vs. diameter^{-1} was confirmed.

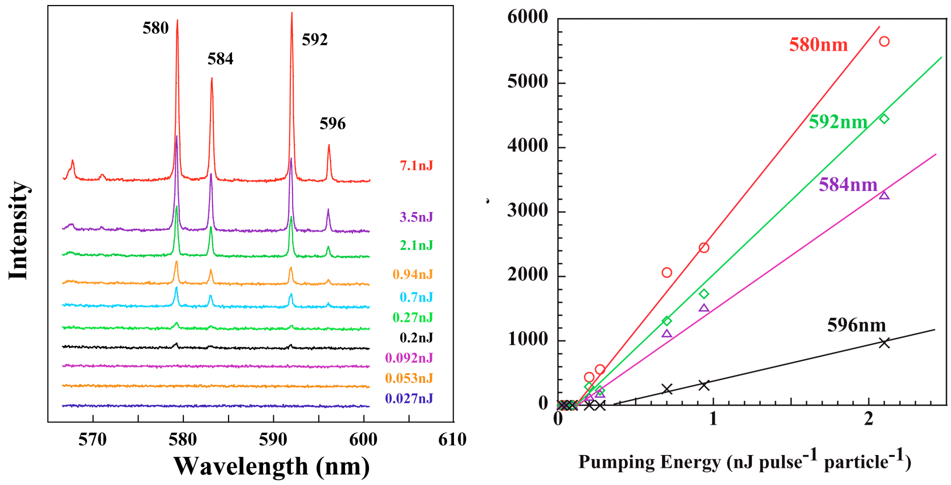


Fig. 6 Emission intensity vs. pumping power.

The wavelength region of the emission peaks were determined spontaneously by incorporated dye content in the spheres, because the overlap region of the absorption and the fluorescence bands did not show the laser emission. Generally, the emission was observed at longer wavelengths than the overlap region. With increasing the R6G content, the emission wavelength region shifted to longer wavelength side, and high-content R6G showed rapid decrease of emission intensity (not shown here). On the other hand threshold intensities also depended on the incorporated dye-content in the spheres. As shown in Fig. 7, threshold intensity decreased with increasing dye content.

In Fig. 8, the emission spectra of different pumping power (10, 3 and 0.8 nJ particle^{-1} pulse^{-1}) were plotted against the shot number (diameter was 6.0 μm and R6G content was 1x10^{-6} mol/g). Low pumping power was suitable to achieve good photostability. Thus, the most stable conditions for lasing of dye-doped spherical particles is obtained by choosing lower dye-content and lower pumping power. In Fig. 9, the typical example of photodegradation is shown for the sample under most suitable condition (DCM-doped particles, pumping: 0.7 nJ particle^{-1}pulse^{-1}). By extrapolation, we know that after 260,000 shot irradiation the emission intensity consumes 50 % of the initial intensity. Since the lifetime (50% consumption of the initial intensity) of laser emission in dye-doped hybrid bulk materials is several thousand pulses [9], [10], the result in Fig. 9 is remarkable.

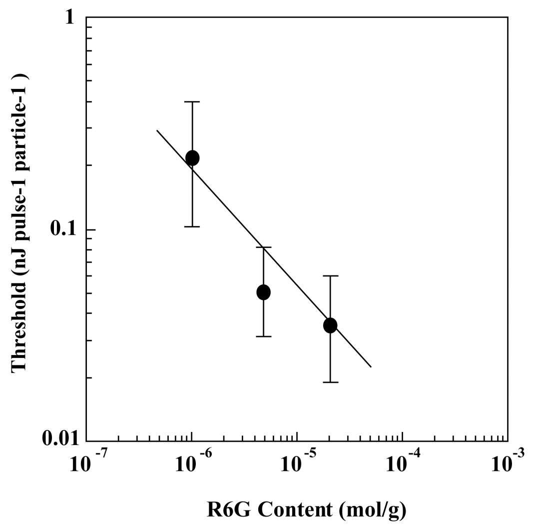


Fig. 7 Threshold intensity of various R6G-content spheres (diameters were 6.2μm).

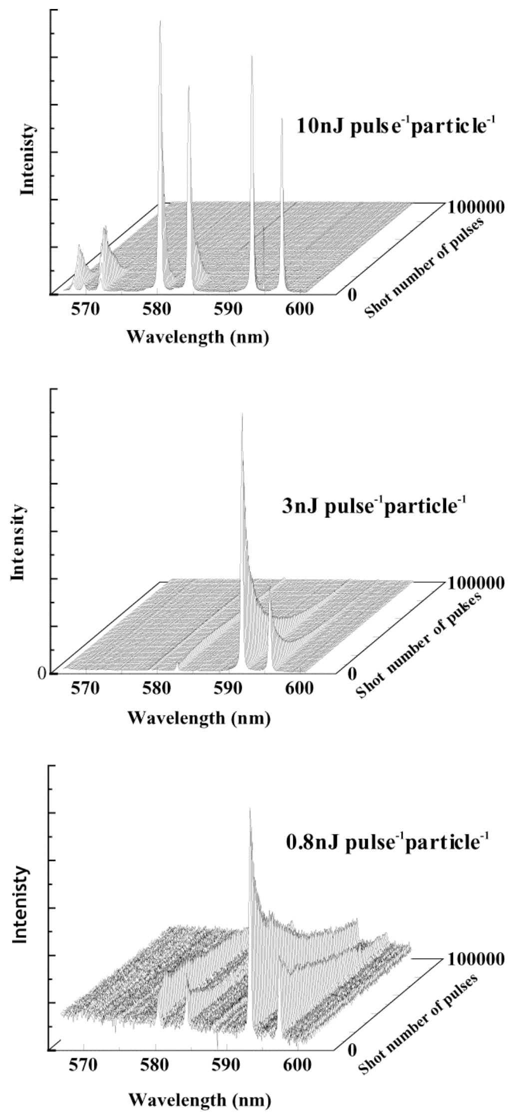


Fig. 8 Photodegradation as a function of pumping power

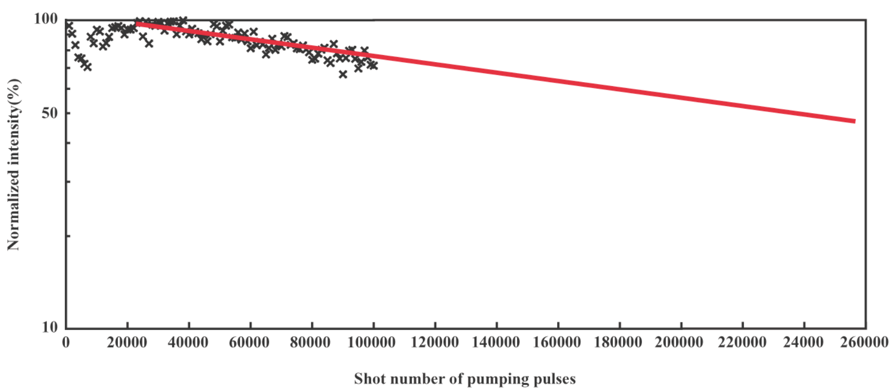


Fig. 9 Change in emission intensity against shot number of pumping pulses

Pumping by an optical waveguide

SEM photograph of an optical waveguide of hybrid materials on silica glass substrate is shown in Fig. 10. Its width and height are 4μm and 12μm, respectively. The composition of hybrid material was MOPS : TMOS : TTIP = 70 : 25 : 5 (mole %), and the refractive index n_D was 1.48. Optical losses of waveguides were measured by the cut-back method, 0.9dB/cm at 633 nm wavelength. For pumping spherical particles narrow width and high height waveguide is desirable. Using the waveguide, pumping of a spherical particle by CW Ar^+ laser (514.5nm wavelength) was carried out.

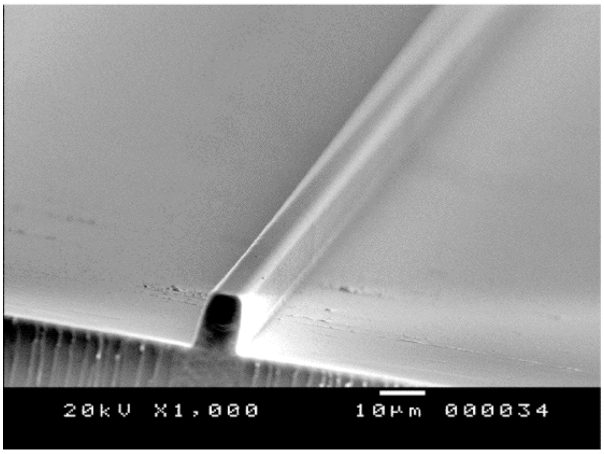
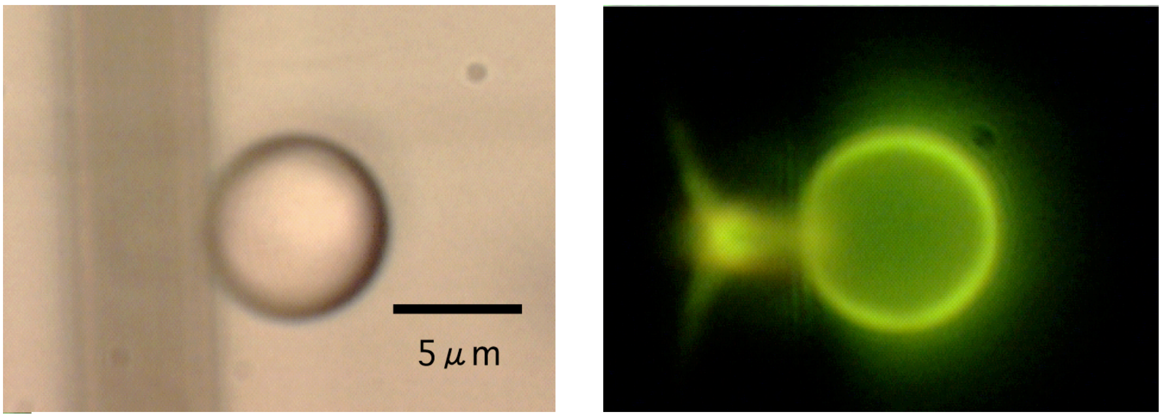


Fig. 10 SEM photograph of an optical waveguide on a silica glass substrate.

In Fig. 11, the photographs of a spherical particle pumped through a waveguide are shown. (Width of the waveguide: 4 μm, and sphere: 7.2μm in diameter, R6G content $1x10^{-6}$ mol/g). The bright ring was observed at the boundary layer of the spherical particle and the surrounding medium (see Fig. 11 (b), where the pumping light was cut by the edge filter), which confirmed the optical resonance effect inside the sphere. The emission spectrum was also measured by CCD detector, and the resonance peaks corresponding to WGM were confirmed [12].



(a) Photograph before pumping. **(b)** Pumped by evanescent wave of the optical waveguide.

Fig. 11 Photographs of a spherical particle placed in contact with an optical waveguide.

4. Discussion

Encapsulation of light in the spherical cavity enables us to lower the threshold intensity of lasing than in the Fabry-Perot type laser structure. As shown in Figs. 7 and 8, "low dye content and low pumping power" is desirable for the photostability. Sometimes, these factors are contradictory each other, because the low-content dye requires the high pumping power for lasing (see Fig. 7). The first notable result of the paper was that under the most suitable conditions, the lifetime (50% consumption) was 260,000 shot pulses (correspond to 7 hrs irradiation).

The second fruitful result in the paper is the performance of pumping spherical particles by an optical waveguide. Practically, plausible set-up for spherical particles of cavity structure will be in the form as shown in Fig. 1. Although direct irradiation of laser light for pumping spherical cavity has been done for convenience in laboratory, the actual coupling efficiency was below few percent of total pumping laser power. Preliminary experiment of light coupling into microsphere through a waveguide showed the hopeful results, as shown in Fig. 11. Coupling efficiency into spherical particles have been investigated using taper optical fibers [13], [14]. Considering their results, the efficiency will be also improved by choosing the optimum parameters: sizes and refractive indices of optical waveguides and microspheres.

To achieve laser emission from spherical cavity, high refractive index difference ($n_{relative}$>1.5) between the microspheres and surrounding medium is inevitable. In the paper, the pumping was carried out in air to meet the requirement of high-index difference. Supposing that we use available low-index materials for cladding (e.g. n_D=1.3-1.4), spheres of n>2.0 are needed to satisfy the high index difference of nearly $n_{relative}$ >1.5. We now have performed that high-index microspheres (n_D>2.0) were fabricated by subsequent heating of high-TTBu-content hybrid spheres [15]. High index microspheres were prepared by the vibrating orifice technique. Resonant emission was confirmed from these Eu^{3+}-doped high-index spheres. Therefore the high-index microspheres enable us to prepare the conventional optical devices cladded with low-index materials. These results will open the new micro-optics for practical applications.

5. References

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