# 論文 / 著書情報
# Article / Book Information

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|---|---|
| Title | Dye-Doped Spherical Particles of Optical Cavity Structure |
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| Citation(English) | Sol-Gel Optics IV, SPIE, Vol. 3136, No. ,  pp. 68-76 |
| 発行日 / Pub. date | 1997, |
| DOI | http://dx.doi.org/10.1117/12.279153 |
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PROCEEDINGS REPRINT
SPIE—The International Society for Optical Engineering

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# *Sol-Gel Optics IV*

**30 July–1 August 1997**
**San Diego, California**

SPIE PROCEEDINGS SERIES
Volume 3136

Box 10, Bellingham, Washington 98227 USA. Telephone 360/676-3290.

# Dye-doped spherical particles of optical cavity structure

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## ABSTRACT

Preparation of micrometer-sized spherical particles containing Rhodamine 6G (R6G) has been investigated for spherical cavity structure. Hydrolysis and polymerization processes of phenyltriethoxysilane (PTES) as a starting material was pursued by observing the change of PTES/R6G in HCl solution with its optical absorption and viscosity. As the polymerization of PTES proceeded, increase of molecular size resulted in change its properties from hydrophilic to hydrophobic, and subsequently the solution separated into two layers of aqueous and organic. Polymerized PTES in the organic layer showed good affinity with incorporated R6G, and high monomer/dimer ratio in particles was achieved. Moreover, using them intermixing of unsuitable particles of submicron size was avoided, because hydrolyzed PTES of small molecular size that is the origin of submicron-sized particles was removed to the aqueous layer. With stirring, titration of diluted droplets containing polymerized PTES was suitable for preparing several micrometer sized particles, and followed by solidification in ammonia water. Degree of the polymerization of PTES and viscosity of liquid droplets were the key factors for determining the properties of R6G-doped spherical particles of optical cavity structure.

**Keywords**: Spherical cavity, Organic-inorganic hybrid matrix, Hydrophilic-hydrophobic property, Dye-doped particles, Formation mechanism, Laser emission from a spherical particle.

## 1. INTRODUCTION

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 [1]. 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) [2], and 10~20 μm plastic particles containing laser dyes [3,4]. Since liquid and organic polymer hosts for spherical particles have lower thermal and photostability, various sol-gel techniques have been investigated by many authors [5,6] for preparing dye-doped inorganic spherical particles. Incorporation of organic laser dyes of relatively hydrophobic property such as R6G into inorganic particles, however, was very difficult [7].

In the previous work, we reported that by sol-gel technique hybrid particles can be made from phenyltriethoxysilane (PTES) as a starting material and their matrix containing phenyl group in -Si-O-Si- structute was suitable to incorporate organic dyes such as R6G into them [8]. After particle formation by the technique, those 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 [8]. Thus, essentially, the obtained spherical particles can meet the requirements for cavity structure of such small sized particles. Unfortunately, however, size distribution of the particles made by the technique was large: Submicron size particles unsuitable to the cavity structure were more than 90 % of the total particle number.

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Quality factor of the cavity (Q value) 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 by excluding those of submicron size is the first target of the study. The lasing efficiency is also influenced by undesirable imperfections such as inside pores and surface roughness of particles. In fact in the lasing trials in ref. 8, from some of the particles of 4~6 μm in diameter performance was difficult. Since through such theoretical considerations [1], precise size control, smooth surface of the particle and monomer dye-doping of appropriate content are major concerns for making spherical cavity structure, understanding of the fabrication process is inevitable for the further progress. In this paper, by aiming at preparing several micrometer-sized spherical particles their formation mechanism was investigated to make highly controlled particles for spherical cavity structure.

## 2. EXPERIMENTAL PROCEDURES

Processing stages for preparing R6G-doped spherical particles are shown in Fig. 1. The fabrication is consisted of two major processes; (a) hydrolysis and polymerization of a starting material, phenyltriethoxysilane (PTES), and (b) particle formation from polymerized PTES in an ammonia water. In the (a) process, hydrochloric acid solution (pH 3) was used to hydrolyze the mixed solution of PTES and R6G. The solution was stirred for 1 ~ 5 days at room temperature. Absorption spectra of the R6G-dispersed solutions at an each step were measured to determine the change in dye contents in separated two layers. Viscosity of sol was measured using Ubbelohde-type viscometer at 30°C.

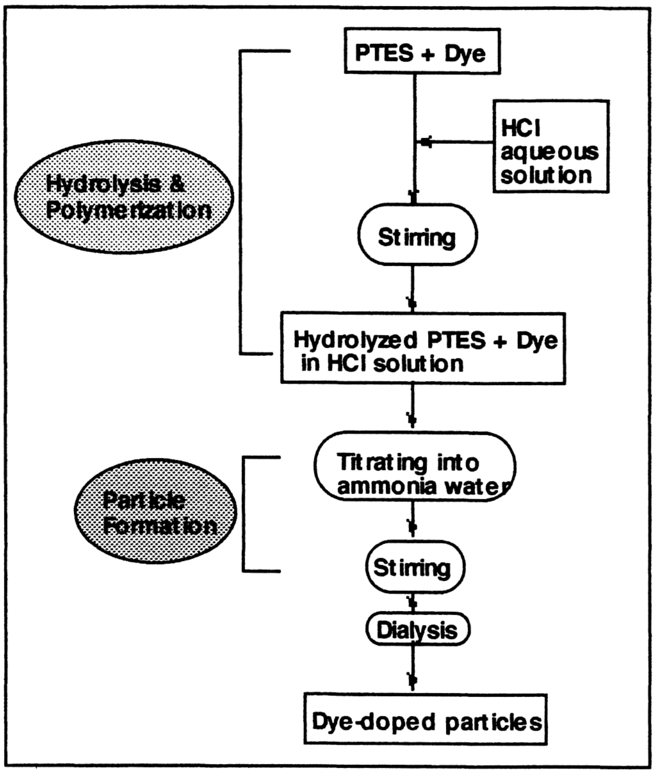


Fig. 1 Processing steps for preparing Rhodamine 6G-doped spherical particles

In the (b) process, uniform solution at stage (B) was titrated slowly into an ammonia water with stirring. Particle size dependency on the stirring speed and the concentration of ammonia water were measured. After separation at stage (C), using the solutions of upper and lower layers, particles were made with no stirring. For preparing particles of 3 ~10 μm in diameter fabrication process was improved: After separation, viscous solution of the lower layer was diluted with alcohol at a certain ratio and titrated with high-speed stirring at 200~300 rpm. Subsequently the solution containing dye-doped particles was dialyzed for 1 day in pure water to remove $NH_3$.

Sizes of dye-doped particles were estimated by a scanning electron microscopy (SEM). Typical dye-doped particles were classified crudely into three ranges by a centrifuge and the dye-content in these particles were measured by their optical absorption measurements.

## 3. RESULTS

Schematic illustration of the hydrolysis and polymerization is shown in Fig. 2. With increasing the reaction time in the hydrolysis and polymerization process (process (a)), the solution changed its uniformity as follows. At starting stage(A), R6G/PTES solution (upper) and HCl aqueous solution (lower) was immiscible. After 1 day reaction with stirring (stage (B)), R6G was dissolved uniformly into aqueous solution involving a small amount of alcohol formed by hydrolysis of PTES. After 3 days (stage (C)) the solution separated again into two layers; upper and lower parts were assigned as aqueous-layer and organic-layer.

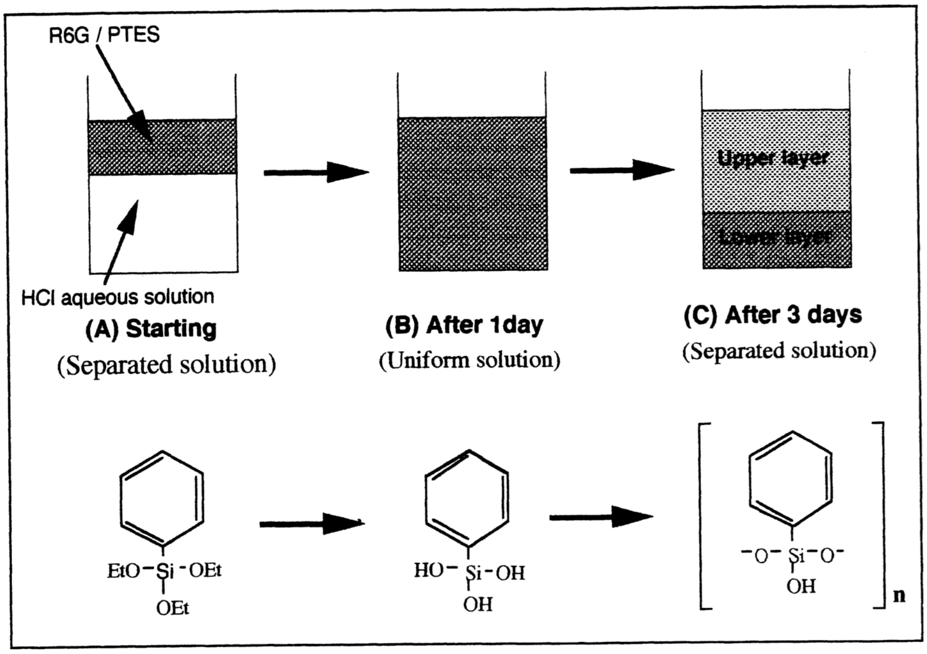


Fig. 2 Schematic illustration for hydrolysis and polymerization process

Viscosity change of the solution is shown in Fig. 3. From stage (A) to (B) the viscosity increased slowly. After the separation, viscosity of the solution in the lower layer increased steeply, but that in the upper layer (does not shown in Fig. 3) kept lower value of 1~2 mPa·s.

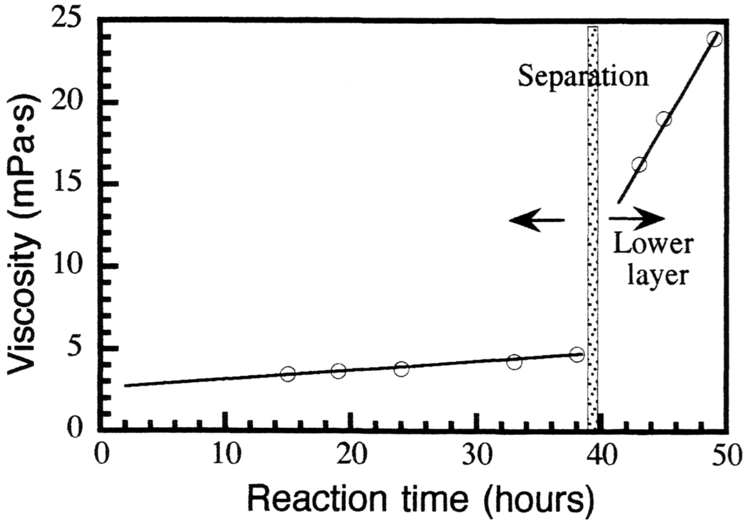


Fig. 3 Viscosity change during hydrolysis and polymerization processes (at 30°C)

Absorption spectra of the upper and the lower layer in the stages (B)→(C) are shown in Fig. 4. Absorption intensities due to R6G decreased in the upper layer and increased in the lower layer with increasing the time, indicating that R6G of relatively hydrophobic property moved from the upper layer (aqueous) to the lower layer (organic).

Schematic illustration for particle formation is shown in Fig. 5. After process (a), solution at stage (B), PTES oligomer containing R6G, was titrated into ammonia water and divided mechanically by vigorous stirring. Average particle size determined by SEM photographs is shown in Fig. 6 as a function of the stirring rate with different ammonia water concentration. Large size particles were obtained with decreasing the stirring rate. Time for solidifying particle depended on the $NH_3$ concentration, higher the concentration makes faster the reaction. For example, rigid particles were formed within 30 seconds at 13 mol /l $NH_3$ concentration. Typical example of particles made from the solution at stage (B) (3.3 mol/l ammonia concentration) is shown in Fig. 7. Particles with various sizes were observed and more than 90 % of total number was submicron-sized particles. The particles used for the lasing demonstration in ref. **8** correspond to those selected from the similar samples in Fig. 7.

Using the solutions of upper and lower layers at stage (C), particles were made with no stirring. As shown in Fig. 8, upper layer aqueous solution gave a lot of small size particles less than 1 μm, and lower layer organic solution with high viscosity gave a large size particle larger than 100 μm. From the view point of spherical cavity structure, submicron is too small and 100 μm is too large.

The separation into two layers, however, works like a "solvent extraction technique". Since (PTES)n of low number n , which is the origin of submicron-sized particles, was extracted into aqueous layer, if the solution of lower layer (organic layer) was used, only higher number of (PTES)n can be supplied. Using this "solvent extraction", fabrication process was improved to prepare particles of 3 ~10 μm in diameter as follows. After separation, viscous solution of the lower layer was diluted with alcohol at a certain ratio and titrated with high-rate stirring at 200~300 rpm. The SEM photograph of the particles is shown in Fig. 9. Number of submicron-sized particles were reduced remarkably by the improved technique.

Measured dye content (mol/g) in classified particles into three ranges (made from the solution at stage (B)) are plotted against nominal values in Fig. 10. Dye content in particles increased with increasing nominal value, but it depended on the particle sizes. Large size particles showed high content. Lasing trial in ref. 8 have succeeded in particles containing dyes more than 2~3 $\times 10^{-5}$ mol/g.

In improved technique, dye content in particles could be also controllable to sufficient value for lasing action, and the monomer / dimer ratio was almost similar to those in ethanol solvent [8].

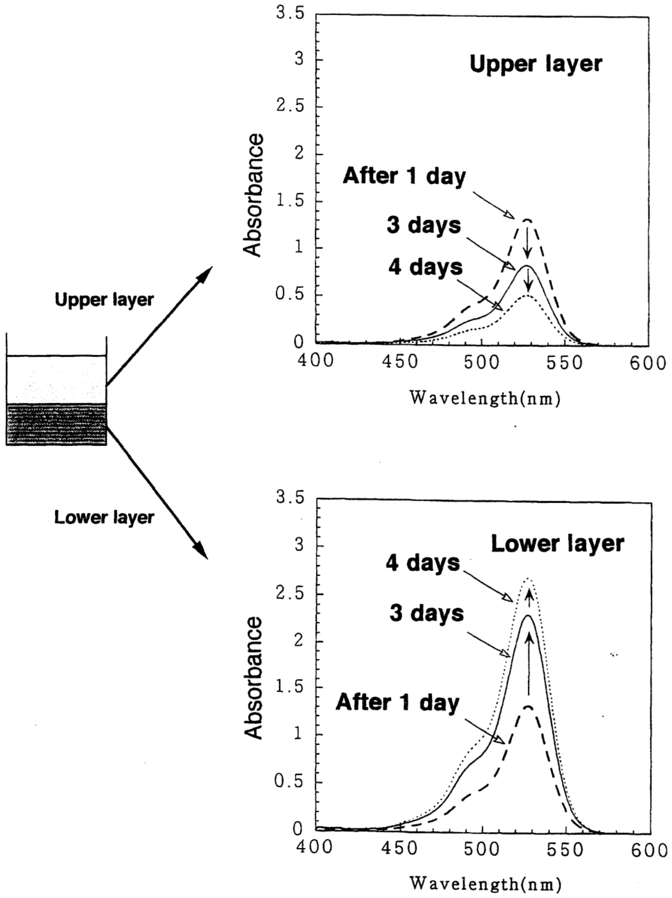


Fig. 4 Change in absorption spectra of the solutions in upper and lower layers from stage (B) to (C).

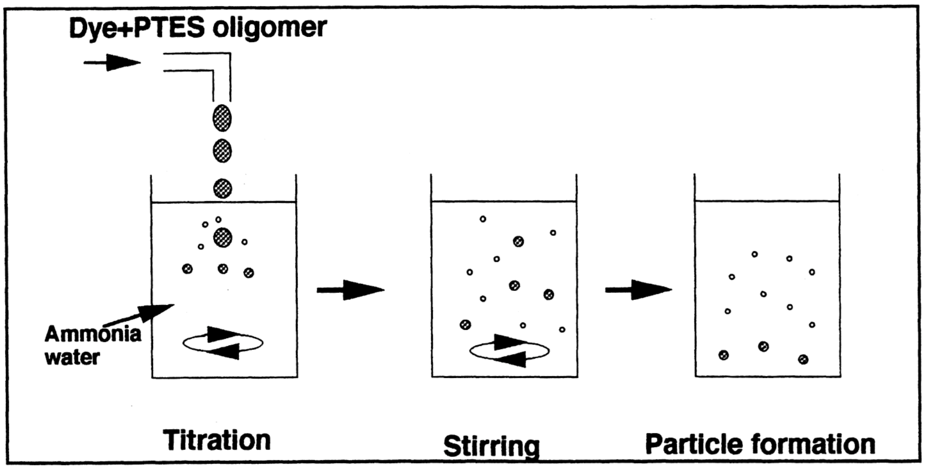


Fig. 5 Schematic illustration for particle formation process

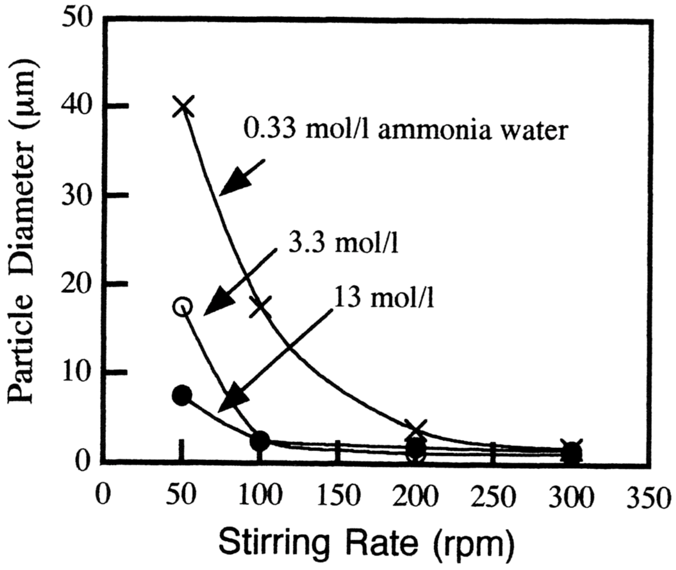


Fig. 6 Average size of particles against stirring rate.

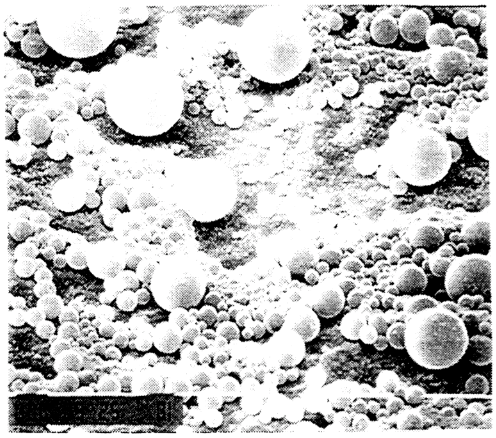
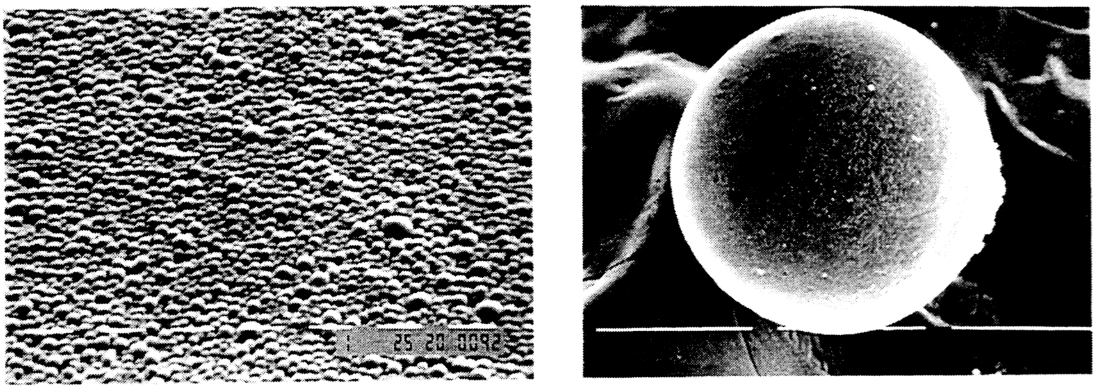


Fig. 7 SEM photograph of particle made from the solution at stage B (Bar : 10 µm)



From upper aqueous solution (Bar : 1 µm ) From lower organic solution (Bar : 100 µm)

Fig. 8 SEM photographs of particles made from upper and lower layer solutions at stage C.

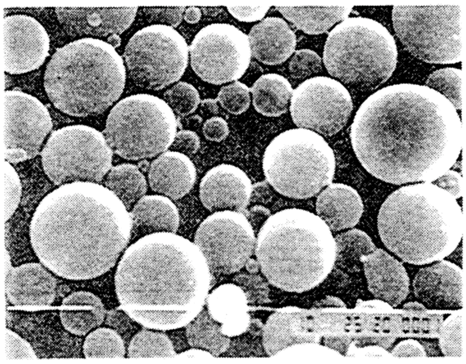


Fig. 9 SEM photograph of particles made by the improved technique. (Bar : 10 μm)

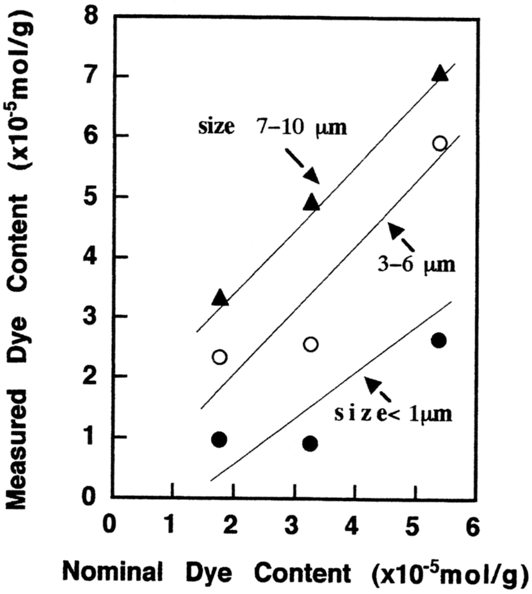


Fig. 10 Dye content in different size particles

## 4. DISCUSSION

Formation mechanism of dye-doped spherical particles applicable to optical cavity was investigated through careful insight into fabrication processes. Essentially this process is considered to be "the emulsion method"; immiscible solution forms droplets in solvent, followed by solidification from their surface. Size dependency on stirring rate and concentration of ammonia water, as shown in Fig. 6, supported this hypothesis. Since high-rate stirring divides a titrated PTES droplet vigorously, small size particles were obtained, and vice versa.

As shown in Fig. 2, in the hydrolysis and polymerization process, hydrolysis occurred first preferentially. Since OH group is major part compared with phenyl group in one hydrolyzed molecule (at stage (B)), they are easily dissolved in aqueous solution. After stage (B), polymerization proceed with increasing the time, oligomers of PTES were formed. Higher degree of polymerization sets up the matrix environment suitable to hydrophobic R6G (stage (C)). This explanation is supported by the fact that R6G molecules moved from the upper layer to the lower layer at stage (C). Schematic illustration for the case of the lower layer at stage (C) is shown in Fig. 11, where an R6G molecule is surrounded by relatively hydrophobic PTES oligomers. The result in Fig. 10, R6G content in the large size particles was higher than that in the small size particles, can also be explained by good affinity between R6G and the PTES oligomer matrix. The good affinity between them also gave high ratio of R6G monomer encapsulated in particles, as we reported previously [8]. The size of particles depend on the degree of the polymerization of PTES: PTES of low number n was easily divided in the ammonia solution, thus small size particle obtained, as shown in Fig. 8 (the left photograph). PTES of high number n (oligomers) gathered each other in aqueous solution, resulting in large size particles more than 100 μm (the right photograph). For preparing several micrometer-sized particles which is more desirable for cavity structure, dilution of the lower-layer solution for lowering its viscosity to 7~10 mPa·s, and dividing droplets by high-rate stirring were necessary (Fig. 9).

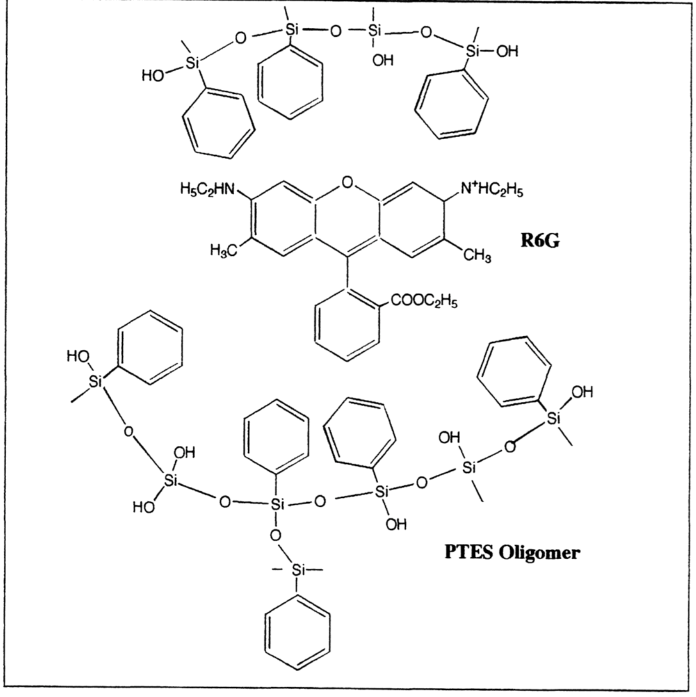


Fig. 11 Schematic illustration of R6G surrounded by PTES oligomers (lower layer at stage (C))

Since lasing with no threshold is expected theoretically in small sized particles of wavelength order, lasing was performed from the particles of relatively small size, 4~6 μm in diameter, as described in ref. 8. Thus, the formation technique described in the issue can meet the requirements for the cavity structure of such small sized particles. Described in detail, however, sometimes submicron-sized open pore was observed by SEM inside the particles at high $NH_3$ concentration, and if there were, lasing from them was very difficult. Furthermore the open pores were often observed in particles of large sizes. These undesirable results reflected the particle formation mechanism that the reaction for solidifying proceeded from their surfaces. For pore-free larger size particles, careful treatments such as particle formation in ammonia water at low concentration will be required for decreasing the reaction rate.

## 5. CONCLUSION

Processing steps for Rhodamine 6G-doped spherical particles were investigated and improved to meet the requirements of optical cavity structure. In the sol-gel process using PTES as a starting material, key points for controlling the particle properties are as follows

(1) In polymerization process, PTES property changed from hydrophilic to hydrophobic with increasing its molecular size.
(2) Polymerized PTES had a good affinity with R6G, thus high ratio of monomer /dimer R6G was achieved in particles.
(3) Separation into organic and aqueous layers can be utilized as "solvent extraction technique" for getting rid of hydrolyzed PTES of small molecular size which is the origin of submicron sized particles.
(4) Titration of diluted polymerized PTES droplets into ammonia water with high rate stirring was suitable to make several micrometer sized particles.
(5) In particle formation, choosing droplet viscosity and controlling of the reaction rate are also the important factors to avoid open pores inside the particles.

The improvements based on the formation mechanism, which was revealed in this investigation, will be useful to make highly controlled particles for spherical cavity structure.

## ACKNOWLEDGMENTS

The authors would like to thank Mr. S. Sakimura and Ms. N. Okada for their help in the experiments. They are also indebted to Dr. K. Kamada for his helpful discussion.

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