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Enhancement of 2-Photon Absorption of a Dye in a Polymer Microsphere Based on an Optical Cavity Effect

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We examined optical cavity effects on the 2-photon absorption efficiency of a dye (Rohdamine B; RhB) doped in polymer microspheres (ion-exchanging resin and poly(methyl methacrylate) (PMMA)). When 1064 nm pulsed-laser light was irradiated on single polymer microspheres doped with RhB under an optical microscope, we clearly observed dye fluorescence from individual microspheres, although the dye was transparent at 1064 nm. We confirmed that the fluorescence intensity was proportional to the square of the laser power for excitation. In contrast, such fluorescence was not observed from RhB doped in a PMMA film, in which the enhancement of a light electric field by an optical cavity effect was never expected. Theoretical calculations indicated that the microsphere possessed several peak values of the quality factor ($Q = 10^2 - 10^5$) at around certain particle diameters under 1064 nm irradiation. This means that the electromagnetic field of incident light is enhanced through light confinement in a microsphere. Based on these results, we conclude that the 2-photon absorption probability of RhB would be considerably enhanced by the optical cavity effects of the microsphere.

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Introduction

One of the recent trends in the fields of nano-photonics and nano-optics is to control "light" and "photons" in a small domain using a specific nanostructure.[1] For instance, a material having a nanometer-sized periodic structure would possess a function to control the propagation of light inside itself. Such a material is called "a photonic crystal" and, in some cases, the crystal can confine light within itself under optimized conditions. In such nanostructured-materials, therefore, light propagation behavior would be restricted specifically, and may result in a nonlinear optical phenomenon, such as multiphoton absorption.

Indeed, Ye *et al*. demonstrated that 2-photon fluorescence of 2-aminopurine was enhanced (120-fold) when the molecules were embedded into a one-dimensional photonic crystal.[2] They attributed the fluorescence enhancement to the high local electromagnetic field of incident light that was generated by a photonic state localized in the defect layer.[3] They also reported a relevant phenomenon: They found an enhancement of dye (Nile blue) fluorescence in a photonic crystal using a total-internal-reflection configuration. On the other hand, Ueno and Misawa *et al*. explored another interesting approach to 2-photon absorption.[4] They fabricated a glass substrate integrated with regularly-structured-gold nano-blocks, and demonstrated that an electromagnetic field would be strongly enhanced (*i.e*., localized surface plasmon) at the nano-gaps between adjacent nano-blocks under light irradiation. Using the substrate, they achieved 2-photon absorption-induced-photo-polymerization of a resin in the vicinity of the nano-gaps by irradiation of incoherent CW light (halogen lamp). Recently, furthermore, we also reported such a plasmon-assisted 2-photon-induced-photochemical reaction and demonstrated that CW near infrared light irradiation could induce a ring-opening photochromic reaction of diarylethene by the assistance of gap-mode plasmon excitation.[5]

These studies imply that a nano-structured material can act as a "vessel" in which 2-photon absorption is considerably prompted. Since multi-photon absorption is a fundamental step in light-energy conversion, such nano-structured materials are quite important for solar energy conversion, photo catalytic reaction, and so on. Hence, it will be necessary to explore and examine other nano-structured materials with respect to 2-photon absorption.

In contrast to such nano-structured materials with complex shapes (photonic crystals and plazmonic substrates), microspheres are a nano-structured material with the simplest shape. In a microsphere, light would be confined inside the sphere and propagate at the sphere/surrounding medium boundary through the total internal reflection of incident light under certain conditions. This propagation of light inside a microsphere is well known as whispering gallery mode (WGM) resonances. Microspheres are characterized by an optical-cavity effect with high quality factors (Q). A high Q value implies efficient confinement of light inside a microsphere (enhancement of a light electric field). Indeed, multi-photon absorption of dopants in microspheres has been reported by many group.[6–12] All of these studies dealt with inorganic materials, *i.e*., up-conversion luminescence from atomic ions (rare earth ions in many cases) doped in glass microspheres. In 1993, we reported 2-photon fluorescence from dye-doped optically trapped single polymer microspheres in aqueous solutions.[13,14] Polymer microspheres have several advantages in terms of optical device applications. It is easy to dope various luminescent species into microspheres by a simple chemical procedure. Also, it is easy

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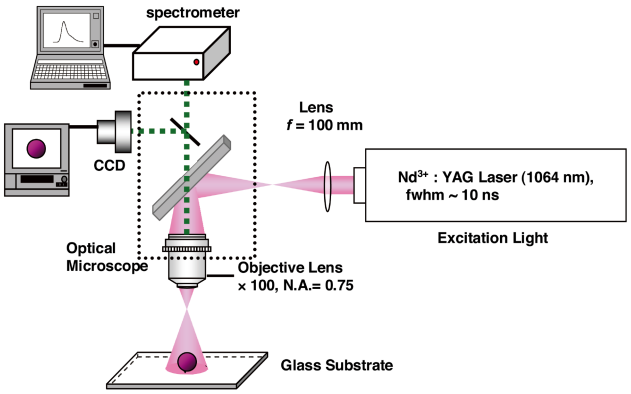

Fig. 1 Optical setup for the experiment of 2-photon fluorescence.

to control the size and to modify the chemical component of microspheres to vary the refractive index. Furthermore, since dye molecules have broad absorption spectra, as compared to those of atom ions, efficient resonant coupling with light would be expected for dye molecules (see text).

However, such studies on 2-photon luminescence from organic microsphere systems have never been reported except for our previous work.[13,14] In the present study, we examined the enhancement of the two 2-photon absorption of a dye doped in polymer microspheres. Visible fluorescence of the dye induced by 1064 nm light irradiation was monitored from single microspheres. Based on such spectroscopic micro-analysis for individual single microspheres, we experimentally confirmed an enhancement of 2-photon absorption in a microsphere system.

Experimental

Polymer microspheres (MCI Gel, an ion-exchanging resin, CK-02A, Mitsubishi Chemical, d (diameter) = 13 μm) and poly(methyl methacrylate) (PMMA, Funakoshi, d = 18 μm) were used as purchased. The microspheres were soaked in an aqueous or acetone/methanol solution of Rhodamine B (RhB) to dope the dye in the sphere. These microsphere solutions were cast onto a glass plate and dried to adsorb the dye-doped microspheres on a glass plate. The concentrations of the dye in individual microspheres were evaluated by absorption measurements under an optical microscope (Optiphoto2, Nikon) to be 20 and 1.0 mM for MCI and PMMA microspheres, respectively. The optical arrangement of the present 2-photon fluorescence experiments is shown in Fig. 1. Under the optical microscope, individual single microspheres were irradiated with a 1064-nm nanosecond pulsed YAG laser (Spectra Physics, Pro-250-10, fwhm ~10 ns) in a defocused mode. The laser power (P) was measured after passing through the objective lens (×40, NA = 0.6). Luminescence from a single microsphere upon 1064 nm excitation was detected by a spectrometer (Hamamatsu, PMA-10) equipped with a microscope through an optical fiber. As a reference, we also studied RhB-doped PMMA films (1.0 mM), in which a cavity effect was never expected. All of the measurements were carried out at room temperature.

Results and Discussion

For a microsphere as an optical microcavity, optical WGM resonance hardly takes place unless a resonant condition is strictly satisfied. For instance, a well-known example of such a resonant phenomenon is a laser (lasing oscillation) using a polymer microsphere doped with an organic dye. In this case, lasing oscillation is readily induced, since a dye molecule generally exhibits a broad fluorescence spectral band. In such a lasing spectrum, we can observe several sharp lasing peaks being superimposed onto the broad fluorescence band. Although the WGM resonant condition is strict, the broad fluorescence band should involve such several sharp bands that can strictly satisfy the resonant condition. In contrast, here we challenged to resonantly introduce pumping beam light (1064 nm) into a microsphere to induce the 2-photon absorption of a dye in the following manner. In this case, the sharp spectral line of the pumping light (1064 nm) must satisfy the resonant condition strictly. One of the aims of the present study is to examine whether such a severe resonant condition is satisfied or not in the present system of a polymer microsphere.

For each individual microsphere, we checked whether it was luminescent or not upon 1064 nm excitation, and we revealed that visible luminescence was clearly observed from a part (~30%) of the microsphere sample. A representative spectrum of the luminescence from a microsphere (MCI doped with RhB) is shown in Fig. 2(a) (black line). The fluorescence spectrum was in good agreement with that of RhB. Figure 2(b) displays the laser power (P) dependences of the fluorescence intensities (I_f) for both the microsphere and film samples. What is important here is that the intensity from the microsphere increases with increasing laser power (P) and I_f is proportional to the square of P (I_f–cP^2). This would indicate that the fluorescence from the microsphere induced by 1064 nm excitation is safely ascribable to the 2-photon fluorescence of the dye. If the light reflection efficiency decreases or the reflected angle slightly changes at each reflection during the WGM traveling of the light in the microsphere, the light reflection would deviate from the total reflection. Such a situation could appear upon by intense laser irradiation due to nonlinear optical effects. If these processes become significant, the relation of I_f–cP^2 will break even in the 2-photon absorption. In the present study, it has been quite difficult to find same other mechanism for fluorescence emission excited by 1064 nm, and 2-photon absorption enhanced by the WGM resonance can be verified by the following discussions.

It should be noted that microparticles whose shape was deviated from a spherical shape (poor sphericity) did not exhibit such 2-photon fluorescence. In contrast, no such 2-photon fluorescence was observed from a film sample, as can be seen in the figure. Also, we carried out experiments on RhB-doped PMMA microspheres, and confirmed analogous results with those depicted in Fig. 2(c). This indicates that the fluorescence enhancement should be ascribed not to specific chemical interactions between the dye and the polymers, but to a physical process arising from the spherical shape. For MCI and PMMA microspheres, 2-photon fluorescence was enhanced by a factor of $>10^3$, as compared to that in the films.

These experimental results clearly indicate that the probability of the 2-photon absorption of the dye at 1064 nm excitation should be enhanced in the microsphere. One possible mechanism to explain this enhancement would be the confinement of 1064-nm-light within a microsphere due to an optical cavity effect. It is worth noting that a dielectric

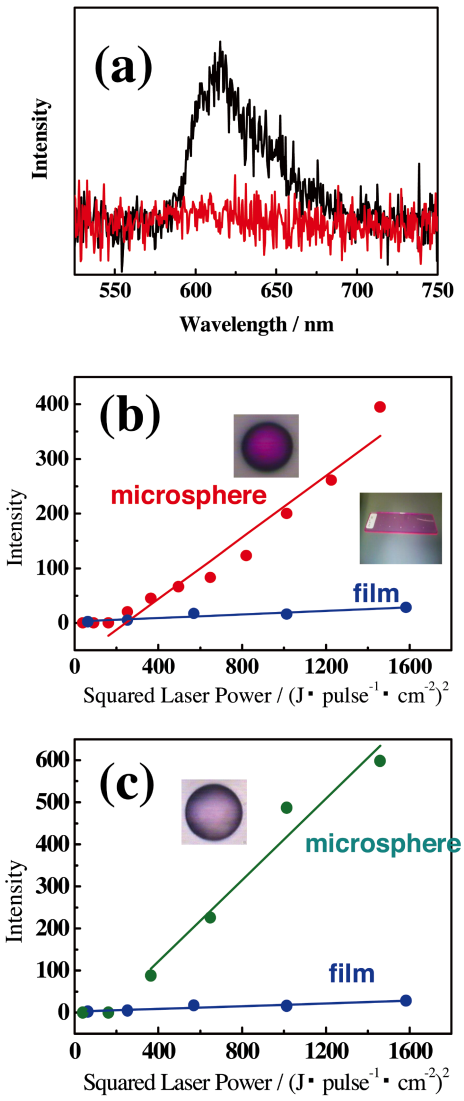

Fig. 2 (a) Black line: a representative example of spectrum of 2-photon fluorescence from the microsphere (MCI). The spectrum is assigned to the fluorescence of RhB. Red line: the RhB fluorescence from the microsphere was completely quenched when it was embedded in PDMS (see text). (b) Laser-power dependence of RhB fluorescence intensity for a MCI microsphere (red line) and PMMA film (blue line). (c) Laser-power dependence of RhB fluorescence intensity for a PMMA microsphere (green line) and PMMA film (blue line).

microsphere often acts as a micro-lens, and this might lead to an enhancement of 2-photon absorption through self-focusing effects.[15] However, the micro-lens effect is denied by the following discussions. First, since 1064 nm irradiation was done with a defocused mode (see Fig. 1), laser light would focus outside the microsphere. Indeed, even if the parallel light irradiates a microsphere, the focus point should be outside the microsphere on the basis of a simple calculation, as follows. The folcal length (f) of a spherical lens (ball lens) is expressed as

$$f = \frac{n}{2(n-1)}R, \quad (1)$$

where n and R are the refractive index and the radius of the sphere, respectively, and f is defined as the distance between

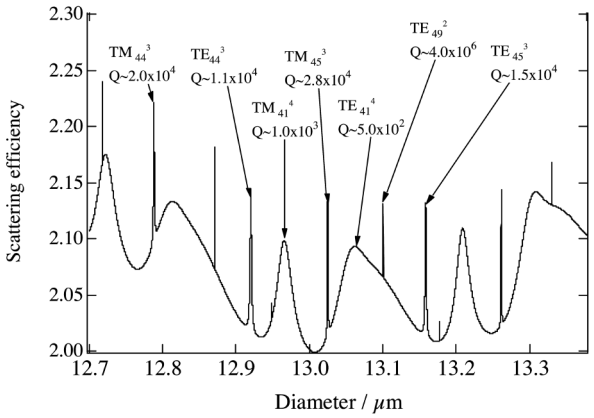

Fig. 3 Simulation for the scattering efficiency and the quality factor, Q, as a function of the diameter for a MCI microsphere.

the center of the sphere and the focal point. In the present case of $n = 1.59$ (described latter), f was determined to be $1.3R$, meaning the focal point outside of the microsphere. Relevant to this problem, we should take the effect of reflection (at the microsphere/air interface) into account. The reflected light could be focused into the inside of the microsphere, which would result in 2-photon absorption. We consider that such a reflection effect would be negligible, since the reflection efficiency is small and the following second reason.

Second, if the microlens effect and/or reflection effect cause 2-photon absorption, all of the RhB-doped microspheres studied should show 2-photon fluorescence under the present excitation conditions. However, about 30% of the microspheres examined here were 2-photon fluorescent, as mentioned before. Thus, the microlens effect is eliminated, and the above discussion indicates that the present microspherical system does not need focusing of the excitation light to induce 2-photon absorption.

In order to examine the effect of optical confinement, furthermore, we carried out simple experiments relevant to index matching. Optical confinement due to the cavity effect would be appreciable when the refractive index of a microsphere is much larger than that of the surrounding medium. In the present case, the refractive index of the microsphere is 1.59 or 1.49 for MCI and PMMA, respectively, and that of the surrounding medium is ~1 (air). For a comparison, we also prepared RhB-microparticle samples embedded in PDMS (polydimethylsiloxane), whose refractive index (n_{ri} = 1.40) was close to that of the microsphere. In this sample (PhB-MCL in PDMS), the optical cavity effect should be strongly suppressed, since total internal reflection of the incident light hardly takes place at the MCI particle/PDMS boundary. This is because the contrast of the refractive index became small. Therefore, 2-photon fluorescence would not be expected. Indeed, as the result shows in Fig. 2(a) (red line), 2-photon fluorescence was never observed from the RhB-microspheres embedded in PDMS.

In addition to these experimental results, a quantitative discussion is necessary to verify the optical cavity effect. Therefore, we calculated the quality factor (Q) of the microsphere under the present experimental conditions. The scattering efficiency of the MCI microsphere was calculated on the basis of Mie scattering theory[16] under the assumptions of n_{ri} = 1.59 and λ = 1064 nm.[17] Figure 3 shows the scattering efficiency calculated for the microsphere with the diameter (d) being around 13 μm, which corresponds to the diameter of the

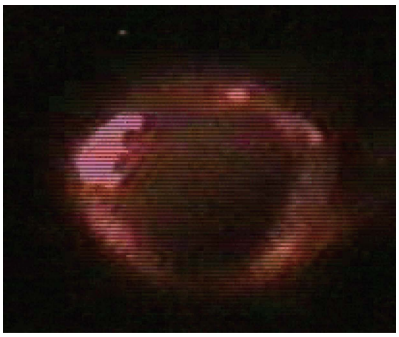

Fig. 4 Representative optical micrograph of the lasing of a MCI microsphere.

microsphere observed under the microscope. The spectrum is composed of a sequence of peaks, called whispering gallery modes (WGMs) and the peaks are indexed as transverse electric (TE_m^l), and transverse magnetic (TM_m^l) modes, where m and l indicate the mode and order numbers, respectively. From the linewidth of each peak, the quality factors (Qs) for these WGMs can be estimated to be $Q = 5.0 \times 10^2$ for TE_{41}^4 and 4.0×10^6 for TM_{49}^2. In addition, the mode spacing between WGMs with adjacent mode numbers and same order numbers was calculated to be about 240 nm in diameter.

To realize the enhanced two-photon excitation process, the microsphere diameter must be appropriately chosen, and one of the WGMs peaks should coincide with the sphere diameter for efficient interactions with the incident laser wavelength. From the spectral linewidth of the incident laser (<1.0 nm), the equivalent linewidth in diameter can be estimated to be about 12 nm, while the sharp WGMs with high quality factors ($Q > 10^4$) have narrow linewidths and large mode spacings in diameter (about less than 1 and 240 nm, respectively), as compared with the linewidth of the incident laser. Since we could not determine the microsphere diameter precisely due to insufficient resolution of the microscope and the size dispersion of the microsphere, the incident laser has a small chance of interacting with one of the WGMs with high quality factors in the experiments, resulting in no enhancement. The simulated Q value as a function of the sphere diameter (d) of the microsphere (MCI gel) is shown in Fig. 3. As can be seen in the figure, the Q value has several peaks around the diameter of the microsphere used in the present study (d ~13 μm); $Q_1 = 2.0 \times 10^4$ at $d_1 = 12.78$ μm, $Q_2 = 1.1 \times 10^4$ at $d_2 = 12.92$ μm, $Q_3 = 1.0 \times 10^3$ at $d_3 = 12.96$ μm (broad peak), $Q_4 = 2.8 \times 10^4$ at $d_4 = 13.03$ μm, $Q_5 = 5.0 \times 10^2$ at $d_5 = 13.06$ μm (broad peak), $Q_6 = 4.0 \times 10^6$ at $d_6 = 13.10$ μm, and $Q_7 = 1.5 \times 10^4$ at $d_7 = 13.16$ μm. Since the shapes of the microspheres should deviate from a real sphere, and possess more or less anisotropy in the shape, some part of the microspheres (~30%) would have WGM whose resonant diameter coincides with coincident to d_1 – d_6 inside itself with various directions of circularly traveling. Only such a microsphere can satisfy the strict WGM resonant condition.

In addition, the WGMs with low quality factors have many chances to interact with the incident laser wavelength, since WGMs with low quality factors (Q_3 and Q_5) have a broader linewidth in the spectrum, as compared with the sharp WGMs. Although the broad WGMs typically cause a weaker enhancement than those with high quality factors because of the low quality factors, these broad WGMs still have quality factors of more than 5×10^2 at $d_5 = 13.06$ μm, and this value is high enough to induce nonlinear phenomena, *e.g.*, laser oscillation. Therefore, the traveling time of incident light in the microsphere would become longer, resulting in an enhancement of the absorption efficiency. We can readily induce lasing of the microsphere by optical pumping with a typical example (optical micrograph) being shown in Fig. 4. This means that the microsphere has high Q values. However, the lasing behavior seen in the figure seems to be somewhat inhomogeneous, although the excitation was done homogeneously, indicating that the microsphere has various WGM with different Q values, as discussed above. A large part (~70%) of the microspheres would not possess a WGM satisfying the resonant conditions (d_1 – d_6), resulting in no 2-photon fluorescence.

The light electric field is enhanced in the microcavity on the basis of the following equation (see Appendix):

$$E(t)^2_{max} = E_0^2(2Q/w_0)^2, \quad (2)$$

where $E(t)_{max}$ is the maximum of the electric field inside a cavity, E_0 is an pre-exponential factor of the electric field ($E(t) = E_0\cos(w_0t)$), and w_0 is the angular frequency of the incident light. According to the equation, the 2-photon absorption efficiency (α_2) of a dye under an enhanced light electric field would be proportional to Q^4 because α_2 should be proportional to the square of the photon density, $(E(t)^2)^2$. This means that even the low Q value ($Q_5 = 5 \times 10^2$) causes increases in α_2 by a factor of 10^{10}. Thus, the 2-photon fluorescence would be enhanced by the optical-cavity effect. Note that even in such an enhancement with a factor of 10^{10}, 2-photon fluorescence is still weak, since the 2-photon absorption cross section is on the order of 10^{-50} cm^2. Other high Q values (Q ~10^4) would also contribute to the 2-photon fluorescence observed in the present study, where 2-photon fluorescence was enhanced in microspheres with a factor of >10^3, as compared to the films.

Conclusion

In conclusion, a microsphere is capable of enhancing the 2-photon absorption of a molecule (dye) doped in a microsphere on the basis of the optical-cavity effect, which increases the Q value. Experimental data and theoretical calculations do not contradict with our conclusions. Microspheres have potential applications to novel reaction fields, in which near-infrared light can drive visible/UV photochemical and photo-catalytic reactions through enhanced 2-photon absorption.

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Appendix

Derivation of Eq. (1)

The definition of a quality factor Q in an optical cavity is

$$Q = wW/P,$$

where w is the angular frequency of light, W energy that is accumulated in a cavity, and P the energy loss from a cavity. Therefore, we can derive the following equation. Then, from $P = -\mathrm{d}W/\mathrm{d}t$, we can express $W(t)$ as

$$W(t) = W_0 \exp\left(-\frac{w}{Q}t\right).$$

On the other hand, W is proportional to the square of the electric field of light (E), $W = cE^2$ (c, const.), the electric field is written as

$$E(t) = E_0 \exp\left(-\frac{w}{2Q}t\right)\exp(iwt).$$

Then, $E(w)$ is obtained by the integral of the above equation,

$$E(w) = \int_0^\infty E_0 \exp\left(-\frac{w_0}{2Q}t\right)\exp[i(w-w_0)t]\mathrm{d}t.$$

From this equation, the square of $E(w)$ (E^2, corresponding to photon density in a cavity) is:

$$|E(w)|^2 = \left(\frac{E_0\frac{w_0}{Q}}{\left(\frac{w_0}{2Q}\right)^2 + (w-w_0)^2}\right)^2,$$

Then, the maximum of E^2 in the cavity is:

$$|E_{\max}|^2 = |E(w_0)|^2 = {E_0}^2\left(\frac{2Q}{w_0}\right)^2.$$

References

1. P. N. Prasad, "*Nanophotonics*", **2004**, John Wiley & Sons Inc.
2. J. Y. Ye, M. Ishikawa, Y. Yamane, N. Tsurumachi, and H. Nakatsuka, *Appl. Phys. Lett*., **1999**, *75*, 3605.
3. J. Y. Ye and M. Ishikawa, *Opt. Lett*., **2008**, *33*, 1729.
4. K. Ueno, S. Juodkazis, T. Shibuya, Y. Yokota, V. Mizeikis, K. Sasaki, and H. Misawa, *J. Am. Chem. Soc*., **2008**, *130*, 6928.
5. Y. Tsuboi, R. Shimizu, T. Shoji, and N. Kitamura, *J. Am. Chem. Soc*., **2009**, *131*, 12623.
6. Y. S. Duan, J. Y. Wang, L. Liu, and Y. Lu, *J. Luminescence*, **2007**, *122*, 456.
7. J. Y. Wang, W. L. Guo, Z. M. Liu, G. Z. Song, L. J. Zhao, C. Z. Zhang, and G. Y. Zhang, *Acta Phys. Sin*., **2002**, *51*, 1861.
8. X. Wang, Y. Bu, S. Xiao, X. Yang, and J. W. Ding, *Appl. Phys. B*, **2008**, *93*, 801.
9. L. Aigouy, Y. De Wilde, M. Mortier, J. Gierak, and E. bourhis, *Appl. Opt*., **2004**, *43*, 3829.
10. G. F. Wang, Q. Peng, and Y. D. Li, *J. Am. Chem. Soc*., **2009**, *131*, 14200.
11. H. Fujiwara and K. Sasaki, *J. Appl. Phys*., **1999**, *86*, 2385.
12. H. Fujiwara and K. Sasaki, *Jpn. J. Appl. Phys*., **2004**, *43*, L1337.
13. H. Misawa, R. Fujisawa, K. Sasaki, N. Kitamura, and H. Masuhara, *Jpn. J. Appl. Phys*., **1993**, *32*, L788.
14. K. Sasaki, H. Misawa, N. Kitamura, R. Fujisawa, and H. Masuhara, *Jpn. J. Appl. Phys*., **1993**, *32*, L1144.
15. S. Lecler, S. Haacke, N. Lecong, O. Cregut, J.-L. Rehspringer, and C. Hirliman, *Opt. Express*., **2007**, *15*, 4935.
16. P. W. Barber and S. C. Hill, "*Light Scattering by Particles: Computational Methods*", **1990**, World Scientific, Singapore.
17. The precise refractive index value of MCI gel is unknown. Since the backbone structure of MCI gel is polystyrene, here we used refractive index value of polystyrene for that of MCI gel.