Studies of whispering gallery modes of single, coated microspheres by steady-state and time-resolved laser fluorescence microscopy

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Abstract. Dye coated single silica and barium titanate microcavities exhibit the whispering gallery modes (WGMs) in their fluorescence spectra. These modes are extremely sensitive to the size, shape and refractive index of the microcavity as well as of the coating thickness (mantle). Theoretical simulations on WGM have been carried out based on the Aden and Kerker model of Lorentz-Mie theory. The effects of the mantle thickness and the surrounding medium on WGMs have been studied. The variation in the decay times of dye molecules with the microcavity size and the mantle thickness have been studied.

1. Introduction

Small optical resonators, of micrometer dimensions with large Q value have diverse technological and scientific applications such as biosensing [1-4], low threshold lasing [5] and enhanced energy transfer [6-10] in the visible region. While undergoing total internal reflection, the electromagnetic wave propagates along the surface to create the standing wave field, known as the whispering gallery mode (WGM). If an atom is embedded or placed in the vicinity of an optical microcavity, its radiative behavior is significantly altered. The Q value and cavity induced rate alteration can be much higher in spherical microcavities than in planar cavities because of the 3D optical confinement.

Chew et al. have proposed the theoretical expressions for the radiative rates of atoms in the vicinity of the microsphere by using classical theory [11] while Klimov et al. have given these expressions by using quantum theory [12]. However, work on coated microspheres is scarce in the literature [13, 14].

2. Experimental

The standard laser dyes rhodamine B (RB) and N, N’-bis (2, 5-di-tert-butylphenyl)-3, 4:9, 10-Perylenebis (dicarboximide) (DBPI) (Aldrich) were used as received. The solvents (methanol and benzene) were obtained from Qualigens Fine Chemicals and Central Drug House Ltd respectively. Silica (Duke Scientific Corp.) and barium titanate (Mo-sci Corp.) microspheres were immersed in the dye solutions (10⁻⁴M) for more than 10 hours. These microspheres were then filtered and dried under ambient conditions for a few hours. After completely drying, the microspheres were transferred to a glass slide for the measurement.

Single microspheres were selected with the help of the epifluorescence microscope (NIKON Eclipse E-400). The excitation source was a He-Ne laser (543.5 nm). The spectra were measured with a combination of a PC controlled spectrograph (Spectrapro 2750, PI Acton) and CCD detector.
Decay time measurements were done with the technique of time-correlated single photon counting (TCSPC) technique [15].

3. Theoretical aspects
The separation between the adjacent WGMs (or free spectral range, FSR) for a coated sphere is approximately given by [14]

\[
\Delta \lambda = \left( \frac{\lambda^2}{2\pi m_1 r_1} \right) \tan^{-1} \left[ \left( \frac{m_1}{m_2} \right)^2 - 1 \right]^{1/2} \left( \frac{m_1}{m_2} \right)^2 \left[ \left( \frac{m_1}{m_2} \right)^2 - 1 \right]^{1/2}
\]

(1)

where \( \lambda \) and \( r_1 \) represent the wavelength of the light and the radius of the microsphere, respectively. \( m_1 \) and \( m_2 \) are the relative refractive index of the core and mantle with respect to the surrounding medium \( (m_{med}) \), respectively (figure 1). Aden and Kerker have [16] solved the problem of scattering from a layered sphere using Mie – Debye theory. The scattering cross section is given by

\[
\sigma_s = \frac{2\pi}{k^2} \sum_{n} (2n + 1) \left( |a_n|^2 + |b_n|^2 \right)
\]

(2)

where \( k \) is the complex propagation constant. \( a_n \) and \( b_n \) are the scattering coefficients.

Figure 1. Schematic of the coated microsphere. Here \( r_1-r_2 \) gives the thickness of the mantle (see text for details).

4. Results and discussion
A small portion of the fluorescence spectrum of a RB coated single silica microsphere of diameter \( \sim 8 \mu m \) is shown in figure 2 (panel A). The observed spectrum matches reasonably well with that obtained from the simulations as indicated in panel B. The mode assignment is done by using the procedure given elsewhere [17].

4.1. Effect of refractive index of the microspheres
The separation between the adjacent WGMs (FSR) decreases with increase in the refractive index of the microspheres. This is shown in figure 3. The WGMs in the fluorescence spectrum of RB coated single barium titanate microsphere \((n \sim 2.1)\) are much sharper than those observed for the case of silica microsphere \((n \sim 1.45)\) coated with the same dye. The \( Q \) values for the barium titanate microspheres are approximately double those of the silica microspheres.

4.2. Effect of refractive index of the surrounding medium and the mantle thickness
Fluorescence spectra of the dye DBPI coated single silica microsphere of size \( \sim 20 \mu m \) surrounded by water \((m_{med} \sim 1.33)\) and air \((m_{med} \sim 1)\) are shown in figure 4. The separation between the WGMs is large in water medium as compared to that in air. This is because the separation decreases with the relative refractive index of the microsphere (equation (1)). The full width at half maximum (FWHM) of the WGMs is found to be larger in water medium as compared to that in air. The \( Q \) value decreases by a factor of 2.6 from the case of water. The ratio of the peak fluorescence to the background fluorescence is 1.9 in air as compared to 1.1 in water medium. The observed \( Q \) value for a microsphere is given by [18]

\[
\frac{1}{Q} = \frac{1}{Q_0} + \frac{1}{Q_a}
\]

(3)

where \( Q_0 \) represents the quality factor associated with the real value of the refractive index while \( Q_a \) is associated with the imaginary refractive index of the microsphere due to the self-absorption. For
thin coatings of the order of a few tens of nm, $Q$ is approximately equal to $Q_0$. For thicker coatings (obtained from the concentrated solutions) the quality factor decreases due to appearance of $Q_a$. This can be seen in figure 5. The $Q$ value as well as the ratio of peak intensity to the background fluorescence decrease nearly by a factor of 3 as the concentration increases from $10^{-4}$ M to $10^{-2}$ M.

![Figure 2](Image)

**Figure 2.** Fluorescence spectrum of RB coated silica microsphere sitting on a glass plate (panel A). Panel B shows the calculated scattering efficiency for a coated microsphere.

![Figure 4](Image)

**Figure 4.** Observed WGMs in the fluorescence spectra of DBPI coated single silica microsphere of diameter ~ 20 µm kept in (a). water (b). air.

![Figure 5](Image)

**Figure 5.** Observed intensities of WGM in the fluorescence spectra of single silica microsphere of diameter 10 µm coated with two different concentrations of dye RB (a). $10^{-2}$M and (b). $10^{-4}$M.
4.3. Cavity effects on the decay times of the RB molecules coated on silica microspheres

The decay profiles of microspheres coated with different concentrations (10^{-3} M and 10^{-4} M) of RB were recorded. The fluorescence intensity (I(t)) exhibits a bi-exponential behaviour

\[ I(t) = B_1 e^{-\frac{t}{\tau_1}} + B_2 e^{-\frac{t}{\tau_2}} \]  \( \text{(4)} \)

where \( B_1 \) and \( B_2 \) are the amplitudes of the fluorescence lifetime components \( \tau_1 \) and \( \tau_2 \) respectively. The fluorescence decay for a coated microsphere of 25 \( \mu \)m diameter exhibits two components viz., 1.3 ns and 3.2 ns, respectively. The fractional intensity of the slow component dominates here. On decreasing the size to 18 \( \mu \)m, the corresponding decay times become 1.6 ns and 3.8 ns, respectively with approximately same fractional intensities. This decrease in the decay time is observed only for the microsphere coated with a lower concentration (10^{-4} M) where the coating thicknesses are of the order of a few tens of nm. Since the quantum yield of RB is close to unity, and there is no other nonradiative process that can appear on reducing the size, this behaviour indicates towards the inhibition of the radiative rate for the smaller sized microcavities. For the microcavity coated with higher concentration (10^{-3} M), the decay times do not change appreciably with the size and are close to the decay times of the single crystal of 8 \( \mu \)m x 13 \( \mu \)m size.

Conclusions

Fluorescence spectra of dyes coated on single microspheres exhibit WGMs. The FWHM of the WGMs are controlled by the coating thickness, refractive index of the microsphere and the medium. Single silica microspheres coated with low concentrations show inhibition of the decay rate at smaller sizes due to thin coatings. High concentration coatings fail to show this effect due to presence of the imaginary refractive index.

Acknowledgement

We thank Department of Science and Technology (DST), New Delhi for financial support.

References

[1] Sandeep P and Bisht P B 2005 Chem. Phys. Lett. 415 15-19
[2] Vollmer F, Braun D, Libchaber A, Khoshisima M, Teraoka I and Arnold S 2002 Appl. Phys. Lett. 80 4057-59
[3] Arnold S, Khoshisima M, Teraoka I, Holler S and Vollmer F 2003 Opt. Lett. 28 272-274
[4] Armani A M, Kulkarni R P, Fraser S. E, Flagun R C and Vahala K J 2007 Science 317 783-787
[5] Spillane S M, Kippenberg T J and Vahala K J 2004 Nature (London) 415 621-623
[6] Druger S D, Arnold S and Folan M 1987 J. Chem. Phys. 87 2649-59
[7] Agarwal G S and Gupta S D 1998 Phys. Rev. A 57 667-670
[8] Pandey K K and Hirayama S J 1996 Photochem. and Photobio. A: Chem. 99 165-175
[9] Kiraz A, Doğanay, Kurt A and Demirel A L 2007 Chem. Phys. Lett. 444 181-185
[10] Fujiwara H, Sasaki K and Mahasura H 2005 Chem. Phys. Chem. 6 2410-16
[11] Chew H 1987 J. Chem. Phys. 87 1355-60
[12] Klimov V V, Ducloy M and Letokhov V S 1996 J. Mod. Opt. 43 2251-67
[13] Shibata S, Ashida S, Segawa H and Yano T 2006 J. Sol-Gel Sci. Techn. 40 379-384
[14] Wang J, Wang M, Liu L, Hao W, Hou B and Lu Y 2007 J. Lumin. 122 949-950
[15] Sandeep P and Bisht P B 2005 J. Chem. Phys. 123 204713-7
[16] Aden A L and Kerker M 1951 J. Appl. Phys. 22 1242-46
[17] Dantham V R and Bisht P B 2008 J. Opt. Soc. Am. B. (in press)
[18] Chýlek P, Lin H B, Eversole J D and Campillo A J 1991 Opt. Lett. 16 1723-25