**Whispering gallery modes in the two-photon luminescence of organic microspheres**

I.A. Kolmychek, N.V. Mitetelo, K.D. Zhdanova, V.B. Novikov, E.A. Mamonov, M. Jyothi, D. Venkatakrishnarao, R. Chandrasekar, T.V. Murzina

1Department of Physics, M. V. Lomonosov Moscow State University
2School of Chemistry, University of Hyderabad, Hyderabad 500046, India

*irisha@shg.ru

**Abstract.** Organic microstructures attract much attention due to their exciting properties that can be introduced by a proper choice of the composition, shape and alignment in an array. Here we apply the nonlinear optical microscopy for the studies of resonant properties of individual response of organic microspheres of various compositions. The observed spectral modulation of the two-photon luminescence spectra of such structures is caused by excitation of the whispering gallery modes (WGMs) that correspond to the two-photon luminescence spectrum of a particular microparticle specimen. Lasing and photobleaching effects induced by intense near-IR laser radiation are discussed.

1. **Introduction**

Intensive studies of microstructures of various design are stimulated by the modern trend in photonics for the search of effective, functional and tunable microelements. It was recognized that one of the perspective ways here is the usage of organic microstructures, which can be made via the self-assembling technique and reveal a number of attractive properties, such as a relatively easy way for the modification of the chemical composition, shape and dimensions, which govern their optical and nonlinear optical response[1]. The ability of this technique for the fabrication of axially symmetric structures allows for the principal realization of the excitation of whispering gallery modes (WGM) and relevant effects. It has been demonstrated that for the case of organic dyes, WGMs can be observed for microstructures of different shapes (μ-spheres, -hemispheres, -frustums, -rods) [2,3] and the quality factor up to several hundred can be achieved.

In this work, we discuss the nonlinear optical excitation of spherical organic microstructures, namely, the two-photon excitation of the photoluminescence and of the WGMs. The main benefit of this approach consists in the usage of a fundamental wavelength that corresponds to the transparency range of most organic specimen, thus providing a large penetration depth, while the irradiation of the resonating microstructures can be realized in the two-photon luminescence range. As the high intensity of the pump laser radiation is required in this case, a number of the nonlinear optical effects should be studied, including the multi-photon excitation and photoluminescence, photobleaching of the dyes, WGMs excitation and lasing.
2. Experimental section
The structures under study are the microspheres made by the molecular self-assembling technique described in detail elsewhere [4] and applied for the red dye (DCM). In this method, an acetonitrile solution of DCM dye (2 mg/2 ml) was sonicated for 30 sec and left undisturbed for 10 min, then a few drops of the solution was dispersed on a clean glass slide under slow solvent evaporation condition (self-assembly process) to form the microparticles. The evolution of spherical shape is associated with surface tension effect. The nonlinear-optical (NLO) effects in individual DCM microspheres were studied by using the NLO microscopy set-up based on a femtosecond titanium-sapphire laser with the pulse duration of 60 fs and the central wavelength tunable in the range 760-860 nm. The pump beam passed through a dichroic mirror was focused on the edge on a microparticle by an objective with NA=0.7, which provided the optical resolution for the NLO signal of approximately 500 nm. The reflected NLO signal collected by this same objective was reflected by the dichroic mirror passed through a spectrometer and was detected by a PMT. A schematic view of the experiment is shown in Fig. 1a. It is worth noting that in these experiments the fundamental wavelengths correspond to the transparency region of the specimen.

3. Results and discussion
Figure 1b shows the results of the modeling of the electromagnetic field distribution in a typical DCM microsphere associated with the WGMs excitation for the mode with the angular numbers m=l. It can be seen that the field is localized in the equatorial plane, the number of antinodes being dependent on the sphere’s diameter, material dispersion etc. So it is clear that in order to observe the resonant modes in the TPL spectra of a sphere, the signal should be detected from the edge of the structure.

This natural expectation was confirmed by the experimental studies of the spectra of the NLO response of individual microspheres. A typically observed spectrum is shown in Figure 2a. The following features should be noted here. First, the shape of the spectrum with the maximum at approximately 560 nm corresponds to the DCM dye. Second, a pronounced modulation of the TPL intensity can be seen, which is associated with the WGM excitation. While the absolute values of these
maxima are not high, they correspond to a strong amplification of the TPL intensity and relevant electromagnetic field circulating within the cavity. According to our estimations, the quality factor of the WGMs is of the order of 200 and increases with spheres diameter.

![Figure 2](image)

**Figure 2.** a) Two-photon luminescence spectrum of a DCM sphere of 7 µm in diameter. (b) TPL map of a single DCM microsphere of approximately 10 microns in diameter.

First experiments on the power dependence of the intensity of definite WGMs show that under proper experimental conditions it demonstrated a fracture that should be associated with the lasing effect. At the same time, a confrontational effect that was observed in DCM structures is the photobleaching of the organic dye, which appears for the area illuminated by the pump beam. A typical TPL image of a microsphere after the illumination by an intense laser radiation (peak intensity of 300 GW/cm², which corresponds to the average power of 7 mW) is shown in Fig. 2 b. It can be seen that the right-hand side of the sphere reveals much less two-photon luminescence intensity due to this effect.

4. Conclusion

Summing up, we demonstrate that DCM-based organic microspheres support the excitation of whispering gallery modes’ in the two-photon luminescence spectral range. The interplay between the photoluminescence and the photobleaching effects determine the luminescent properties of these organic microresonators excited by an intense laser radiation.

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