Optical second harmonic generation and two-photon luminescence in organic microstructures

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Abstract. We studied optical and second order nonlinear optical effects in arrays of frustum-shaped microstructures composed of orange-red dye by self-assembling technique.

1. Introduction

Nowadays photonics of micro- and nanosized structures attracts much attention of researchers. This is mostly due to high perspectives for application of such types of structures in optoelectronic devices. Most of the studies are carried out for metal structures, which reveal the enhancement of optical and nonlinear-optical effects enhancement due to local field amplification close to plasmon resonances. This was demonstrated for plasmonic nanostructures, nanoantennas, in plasmonic crystals etc. [1], [2]. Organic nano- and microstructures, being dielectric, are attractive because of a number of unique properties connected with possibility to excite different types of Mie resonances in the visible-near IR spectral range, high and tunable refractive index, a way for the modification of their size and shape.

The easiest method for the composition of organic structures is the application of self-assembly technique, which allows the production of structures with different shapes. This has been demonstrated for the composition of microstructures in the form of empty tubes, hemispheres, spheres etc. Due to a specific design, these structures can be applied as optical cavities, waveguides and microlasers, as was shown in a number of papers [3], [4]. Though microstructures made of organic materials are less stable than those based on inorganic ones, their main feature is a relatively simple way for the manipulation of their linear and nonlinear optical properties by a proper choice of their the chemical compound and composition within a structure. Still a number of nonlinear optical effects were observed for organic microrods, such as two-photon absorption and luminescence, and second harmonic generation [7-9]. The effects were quite pronounced due to a strong localization of the fundamental radiation field inside the microstructures, which increased the light-matter interaction.

In this paper, the second-order nonlinear optical response of an array of nonlinear organic microstructures is studied. We show that an enhancement of the second harmonic generation and two-photon luminescence is attained as compared to homogeneous thin films of the same chemical composition.

2. Samples and experimental setup

2.1. Samples

Samples under study are irregular arrays of frustum-shaped organic microstructures fabricated using the self-assembly technique. The details of the samples’ fabrication are discussed elsewhere [3]. In brief, the acetonitrile solution of the nonlinear non-centrosymmetric molecules of a red-orange dye, namely, (E)-2-(2-(4-(4-bromophenyl)(phenyl)amino)styryl)-6-tertbutyl-4H-pyran-4-ylidene)malononitrile, is deposited on a glass substrate. The evaporation of the solvent results in the formation of a set of frustum-shaped particles oriented in such a way as is shown in Fig. 1. It is worth noting that such a uniform orientation of
frustum-shaped microstructures is rather important for any type of potential applications, and is definitely an advantage of the composition method. The typical upper diameter of a frustum particle is about 2 μm and the opening angle is about 45°. The typical distance between the microstructures is several microns and is larger than their average diameter.

It was shown previously [3] that such a specimen reveals the absorption band at the wavelengths smaller than 500 nm and a luminescence in the spectral range of approximately 550-700 nm.

2.2 Experimental setup

Prior to the nonlinear-optical studies, linear optical absorption and luminescence spectra were measured when using the diode lasers operating at the wavelengths of 405 and 532 nm, the power of the incident radiation was about 1 mW. Both transmission and reflection schemes were used. For the nonlinear-optical measurements, an experimental set-up was used based on a Titanium-Saphire laser tunable in the wavelength range from 740 nm up to 890 nm, with the pulse duration being 100 fs and the pulse repetition rate of 80 MHz. Its average output power was varied from 1 mW up to 200 mW. The scheme of the experimental setup is shown in Figure 2. In order to eliminate the influence of the instability of the laser, the intensity of the nonlinear optical response of a sample was normalized to that attained in the reference channel where a crystalline quartz plate used as a source of the nonlinear optical signal. The spectrum of the nonlinear response, that is the two-photon luminescence (TPL) and second harmonic generation (SHG), was analyzed by a monochromator and detected by the photomultiplier Hamamatsu R4220. The laser beam was focused on the sample into the spot with the diameter of 50 μm. The maximal peak intensity of the fundamental beam was 10 MW/cm².
3. Experimental results and discussion

3.1 Linear-optical measurements
Figure 3 shows the photoluminescence (PL) intensity spectrum emitted by the array of the microstructures under the excitation by the CW laser source of the wavelength of 405 nm and 532 nm, the average power being of 1 mW. This relatively low power level was chosen in order to prevent the destruction of the material of the microparticles. Due to the chosen laser beam spot diameter on the sample several dozens of the microstructures were illuminated simultaneously, all of them having small deviations of their size and shape from the averaged values for the ensemble. Thus the PL did not reveal a set of high-quality peaks associated with the excitation of whispering gallery modes that were observed for individual microparticles [3, 8, 9].

![Figure 3. Spectra of the linear (single-photon) luminescence of an array of microstructures obtained for the excitation wavelengths of 405 nm and 532 nm.](image)

Nonlinear optical studies
Typical spectra of the nonlinear optical response measured for various wavelengths of the Ti-sapphire fundamental radiation are shown in Figure 4. The spectra reveal two main features: a wide intensity peak centered at approximately 560 nm, that corresponds to the two-photon excited luminescence, and a smaller in amplitude peak associated with the second harmonic generation. Interestingly, the relative amplitude of this peak depends on the fundamental wavelength.

![Figure 4. Spectra of the intensity of the nonlinear optical response of arrays of frustum-shaped microstructures measured for the fundamental wavelengths of 830 nm (a) and 890 nm (b), the power of the fundamental beam being 25 mW.](image)
In order to study this in more detail, a 3D excitation-emission dependence was measured, which is
shown in Figure 5. It can be seen that the highest values of the intensity of the two-photon luminescence
is attained closer to the spectral boundaries of the fundamental wavelength tuning. The SHG response,
while being much less intensive, also appears and follows the wavelength of the fundamental radiation. It
is more pronounced for the longer wavelengths of the fundamental radiation, which is probably connected
with the efficiency of the two-photon absorption along with the increase of the SHG escape length. The
latter is determined by the absorption spectrum at the SHG wavelengths.

![Figure 5. Emission – excitation scattering matrix of the intensity of the nonlinear optical response of
an array of frustum microstructures. The dependence was measured for a constant value of the
incident power of the wavelength tuned in the range 750-900 nm.](image)

We performed as well the comparison of the efficiency of the nonlinear optical (NLO) response for a
homogeneous orange-red dye of the same chemical composition as was used for composition of the
frustum-shaped microstructures. It was found that in the case of microstructures the scattered nonlinear
optical signal is about 10 times higher as compared to that from an array of frustum-shaped
microstructures. This should be attributed to the local field effects expected for the case of organic
microstructures with high value of the refractive index, which brings about strong field localization
effects.

An important feature of the interaction of a laser beam with a random array of micron-size structures
is the scattering diagram of the nonlinear optical response. In order to study these features more precisely,
we measured the nonlinear optical signal (NLO) scattering indicatrix, the corresponding dependencies are
shown in Figure 6. Here the averaged NLO intensity is plotted, which contains both the SHG and the two-
photon excited luminescence intensity. The incident beam was directed along the normal to the substrate
to the sample and the transmitted intensity was registered. The NLO signal is scattered in a wide angular
range, with the maxima at approximately ±60°. This is probably connected with the geometry of the
microstructures that are oriented in a uniform way. The exact mechanism of this NLO scattering is to be
studied further.
Summing up, we observed that under the excitation by a near-IR femtosecond pulsed radiation the array of micron-size organic frustum-shaped particles exhibits a strong nonlinear optical response, which consists of the two-photon luminescence and optical second harmonic generation scattered over a broad angular range. The emission-excitation spectra shows that the most intense NLO output corresponds to the input wavelengths of 750-770 nm, which is mostly attributed to the highest two-photon absorption in this spectral range. The SHG maximum reveals the opposite dependence, the highest SHG amplitude relatively to the two-photon luminescence was observed for longer wavelengths that shows that in that case larger escape length at the SHG wavelength is the dominant parameter.

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