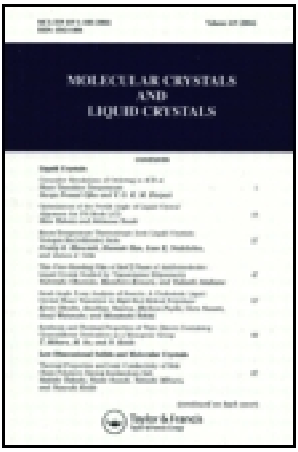

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Nanophotonics: Nanoscale Optical Interactions

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Nanophotonics: Nanoscale Optical Interactions

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Abstract: Nanophotonics defined as nanoscale optical science and technology is a new frontier, which includes nanoscale confinement of radiation, nanoscale confinement of matter, and nanoscale photophysical or photochemical transformation. Selected examples of our research work in each of these areas are presented here. Nonlinear optical interactions involving nanoscale confinement of radiation is both theoretically and experimentally studied using a near-field geometry. The effort in nanoscale confinement of optical domains is focused to control excitation dynamics and energy transfer as well as to produce photon localization using nanostructured materials, rare-earth work on doped glasses and novel inorganic-oganic photorefractive nanocomposites are presented. Spatially localized photochemistry using a near-field two-photon excitation is being developed for nanofabrication and nanoscale memory.

Keywords: Nanophotonics; Multibranched structure; Photonic crystals.

INTRODUCTION

Emerging as one of the most the exciting realms of science today is the field of nanophotonics. Defined as the study of optical phenomena and technology occurring at the nanoscale, nanophotonics deals with processes and structures which are spatially localized in domains smaller than the wavelength of visible radiation.

In recent years much more efforts have been focused on studying nanoscale optical interactions and preparing nanostructured optical materials. Due to the fact that near-field optical microscopy overcomes the diffraction limit, it is now possible to probe the optical interactions at nanoscopic region. Furthermore, the higher degree of precision and resolution offered by near-field optical microscopy also makes it a potential candidate in the photoprocessing and photofabrication. Recently, nanosize control of the local structure has also emerged as a frontier area of material research, which provides an opportunity to manipulate excitation dynamics as well as to influence energy transfer. Nanostructure multibranch and dendritic structure; inorganic: organic hybrids; nanomers; nanoparticles and nanocomposites are opening up new directions for nanophotonics and nanoelectronics.

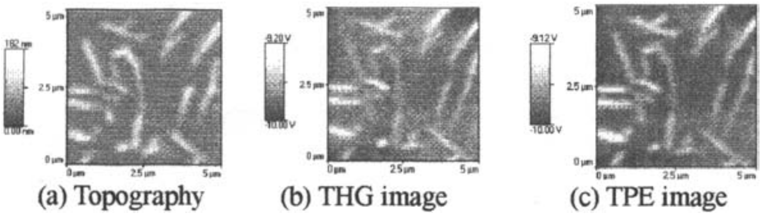
Our approach utilizes nanoscale confinment of radiation, nanoscale confinement of matter and nanoscale photophysical or photochemical transformation to investigate nanoscale matter-radiation interactions [1]. Selected examples of our studies in each of these areas include: (1). nonlinear optical interactions involving nanoscale confinement of radiation probed both theoretically and experimentally using a near-field geometry, (2). Nanoscale confined optical domains used to control excitation dynamics and energy transfer and to produce photon localization. These are illuminated using multibranched structures, nanoparticles, photonics crystals and nanocomposites, and (3). Spatially localized photochemistry using a near-field two-photon excitation for nanofabrication and nanoscale memory. Our focus has been the use of near-field techniques and localized spectroscopy to probe nonlinear optical effects in nanodomains [2].

Nanoscale third harmonic generation and two-photon excitation

A more recent study of $\chi^{(3)}$ effects in nanocrystals of 4-(N,N)diethylamino β-nitrostyrene (DEANST) has used near-field microscopy and localized spectroscopy. We have demonstrated simultanious observation of both third harmonic generation and two-photon excited up-converted fluorescence in nanocrystals of diameter ~200 nm [3]. The nanoscopic domains exhibit centrosymmetry (no SHG) and the $\chi^{(3)}$ manifestations: both THG and two-photon excitation and show local in-plane anisotropy. Collection-mode near-field scanning optical microscopy and spectroscopy are used for studying third-harmonic generation and two-photon excitation in organic crystals. A Q-switched Nd: YLF laser is used as an excitation source. 4-(N, N-diethylamino)-β-nitrostyrene (DEANST) is used as the sample. Nanocrystals of DEANST are prepared by spin coating a drop of dilute ethyl acetate solution of DEANST across a cover slip, and grown by solvent evaporation.

Figure 1(a) shows a 5μm × 5μm topographic image of some as-grown needlelike DEANST crystals. The corresponding THG and TPE images for the horizontal polarization are presented in Figures 1(b) and 1(c), respectively. The intensity variations of THG and TPE are correlated with the topographic features. The fine resolution offered by the present near-field THG and TPE microscopy is about 60 nm, which is better than $\lambda/18$, where λ is the illumination wavelength. The uniform third-harmonic and two-photon intensity distributions along the crystals as shown in THG and TPE images suggest that the lateral distribution of $\chi^{(3)}$ is homogeneous and the molecular orientations are well maintained for each crystal. The difference in both THG and TPE intensities among different crystals results from the difference in crystal orientation.

Near-field spectroscopic study was also performed on individual DEANST crystals. At sufficiently high excitation intensity, simultaneous THG and TPE are observed. No THG-induced fluorescence is generated, which indicates that although bulk DEANST crystals exhibit weak absorption in the ultraviolet region [4], such absorbance is negligible for the DEANST crystals whose thickness are on the nanometric scale. The spectrum also demonstrates that no second-harmonic wave is generated and the THG obtained in DEANST crystals results from the direct third-order nonlinearity $\chi^{(3)}$. In a DEANST molecule, the first hyperpolarizability β appears due to the noncentrosymmetric molecular structure; however, the local spectrum indicates that the DEANST molecules crystallizes in a centrosymmetric structure on a subwavelength scale, which leads to a virtual complete cancellation of second-order effect.



(a) Topography (b) THG image (c) TPE image

Figure 1. (a) Shear-force image, (b) and (c) near-field THG and TPE images of DEANST crystals with horizontal polarization. The arrows show the path across two neighboring crystals used for resolution measurement.

Multibranch bridging structures

Multibranched structures can be produced with varied topology where each arm and the central bridge unit can provide a specific photonic function. They can be prepared with different donor, acceptor groups in specific order and with different bridging groups with through conjugation or segmented conjugation. These structures can also permit photon harvesting by multiarms over a broad range to funnel the energy into the central segment for lasing, amplification and imaging.

Here we present a specific example of a novel multibranch system designed and synthesized at our Institute [5]. This structure labeled as ET-101 is shown below. For comparison the arms, labeled as PRL-501, and the thiophene containing bridging unit, labeled as PRL-406, were also studied and their structures are also shown in Figure 2.

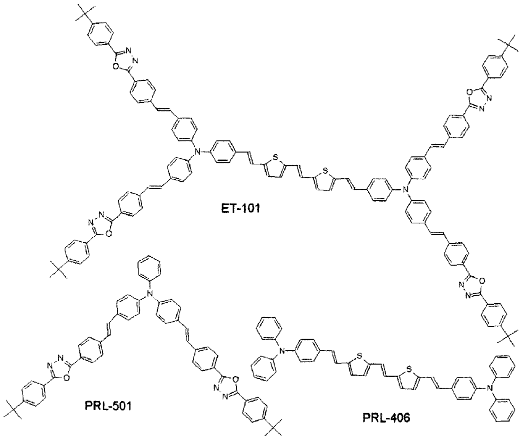


Figure 2. Chemical Structures of ET-101, PRL-501 and PRL-406.

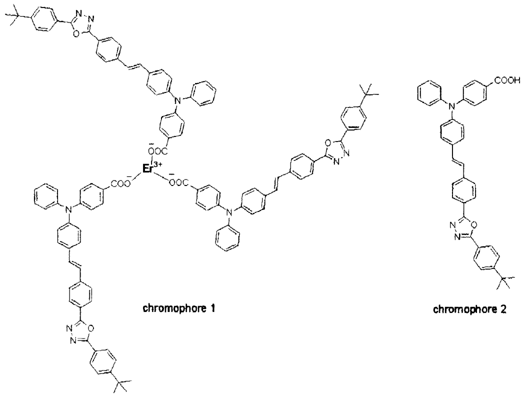
These molecules were characterized for their linear and two-photon properties by using their THF solutions. For two-photon absorption, the Z-scan technique using femtosecond pulses at 800 nm was used. The linear absorption peaks for PRL-501 and PRL-406 are respectively at 417 nm and 457 nm. The linear absorption spectra of ET-101 can be attributed to be derived from both PRL-501 and PRL-406 sub- units. The fluorescence of PRL-501 is strong, in the green region, with a peak at 497 nm. PRL-406 exhibits a weak emission at

554 nm. The multibranched structure exhibits an emission peak basically at the same place as in PRL-406, indicating an efficient energy transfer from the arms (PRL-501 type excitation) to the bridge segment (PRL-406 unit).

Inorganic:organic hybrid multibranched structures

Another exciting direction in materials design is inorganic:organic hybrid structures where multiphoton absorption can take place both in organic and inorganic units. Rare-earth ions are known to exhibit strong multiphoton absorption processes through sequential excitation. Organics provide direct (simultaneous) two-photon absorption.

Here we discuss a specific example investigated at our Institute. This multibranched structure, chromophore 1, was synthesized via ionic interaction of Er^{3+}, with the carboxyl functional group of a two-photon dye, chromophore 2 [6]. The structures of chromophore 1 and chromophore 2 are shown in Figure 3. The optical properties of chromophores 1 and 2 were investigated in THF solutions.



chromophore 1

chromophore 2

Figure 3. Structures of Er^{3+} two photon dye salt (chromophore 1) and the two-photon dye (chromophore 2).

Using the corresponding two-photon dye monomer acid (chromophore 2) as a reference material, we observed that the photoluminescence of the erbium two-photon dye salt (chromophore 1) was significantly quenched while nonlinear absorption (useful for optical limiting) for infrared nanosecond excitation was enhanced compared to the monomeric form. On the other hand, femtosecond Z-scan measurements suggest the same two-photon absorption coefficient for the dye in both forms. A possible explanation is that the presence of erbium enhances the intersystem crossing rate and that the nonlinear absorption effect for nanosecond pulsed excitation must be due to both two-photon absorption and subsequent triplet-triplet excited state absorption. Our analysis of the nonlinear absorption (power limiting) data suggests that the intersystem crossing rate is three orders of magnitude larger for the erbium two-photon dye salt compared with that in the monomeric form.

Photonic crystals

Three-dimensional periodic dielectric structures in which the refractive index varies on length scales of order of the optical wavelengths have recently attracted much theoretical and experimental attention. An especially interesting class of such structures are photonic bandgap (PBG) crystals. For the range of frequencies defined by the PBG, no light can propagate through the crystal in any direction. Instead, light in this frequency range is localized. This has a significant impact on the spontaneous emission of excited molecules placed inside the photonic crystal. If the transition frequency of excited molecules is adjusted to the frequency range of the gap, spontaneous emission of light into unwanted modes can be completely inhibited. This may allow the development of thresholdless lasers.

Our photonic crystals were fabricated from polystyrene spheres with a diameter of 200nm and then infiltrated with coumarin 503 dye. The long-range order of the particles inside the crystals manifests with almost 0 % transmission in the minimum of the stop-gap. The crystals exhibit stop gaps ranging in size from 1-3% of the gap center frequency. Two-photon excited fluorescence spectra of the dye in a photonic crystal were obtained by exciting it with a mode-locked Ti:Saphire laser at a wavelength of 800nm. The direction of the laser light was perpendicular to the surface of the sample. Two-photon excited upconverted emission spectra of coumarin 503 in polystyrene/methanol PC. The diameter of pol. particles d = 200 nm perpendicular to the surface of the sample.

We collected spectra in the reflection mode. For two-photon excited emission spectra of cumarin 503 in our structure, we noticed that, besides filter effects similar to those reported for transmission of external plane waves, also, a sharp maximum appeared [7]. This maximum seems to be a result of amplification of light inside the photonic crystal. The position of the sharp maximum depends on the position of stop gap. Outside the stop gap the shape of emission spectra from coumarin 503 are very similar in case of polystyrene/methanol and polystyrene/DMSO structures. Both spectra also overlap very well with rescaled reference spectra. The amplification of light (sharp maximum) was not noticed for the same coumarin 503 solution in a reference spectrum. Attenuation minimum as well as amplification like maximum appear only in the stop gap region of our photonic crystals.

In our case, the threshold for the laser emission was not yet reached since the magnitude of the maximum was relatively small. However the influence of the photonic stop gap on the emission spectrum is noticeable since the maximum does not appear in the reference spectrum. It also suggests that even more dramatic enhancements may be expected in more strongly scattering photonic crystals.

Nanoscale optical memory with two-photon excitation

Nanoscale optical storage has been carried out on magneto-optic and phase-change media recently [8]. In our experiments, a spatially localized photochemical reaction, induced in a near-field geometry, is demonstrated with both one-photon and two-photon excitation on a nanometer scale and used for nanoscale optical memory and nanofabrication [9]. A dye-doped polymer film (AF-380/PVP) was prepared as the recording medium. Nanoscale domains result when the irradiated dyes are photobleached after being exposed for longer than 10 seconds. These areas show up black due to the loss of fluorescence, and are clearly distinguishable from the surrounding fluorescent areas. This difference in fluorescence intensity is easily detectable and can be used to represent 1 and 0 in recording.

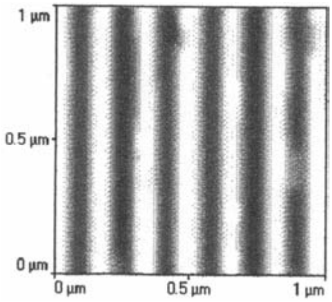


Figure 4. Fine grating structure fabricated with near-field two-photon excitation.

The spatial localization of photobleaching depends on the probe size and intensity distribution of the local field. With one-photon excitation, photobleaching is linear and occurs in the entire zone of illumination. Consequently, relatively large data bits form. However, this can be improved by nonlinear photobleaching with two-photon excitation, because the quadratic dependence of two-photon excitation on light intensity limits the effective excitation to a small volume and enhances the local field confinement in the vicinity of the probe. Figure 4 shows the image of the stripes recorded with two-photon excited photobleaching. The width of a written line is 80 nm, with adjacent line spacing of 160 nm. This result implies that a fine grating ruled with 6250 lines/cm is available with near-field optical technique.

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