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Starch: Application of biopolymer in random lasing

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ABSTRACT

Here we report on the possible application of starch as a dye-doped biopolymeric matrix designed for random lasing generation. Gelatinized biopolymer doped with Rhodamine 6G was used as light amplification medium as well as source of positive feedback which is originating from high surface roughness fluctuations. It is demonstrated that, applying the starch as a matrix for laser dye we can significantly increase photostability of laser emission with respect to other biopolymeric based systems which is great advantage of this material.

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1. Introduction

Starch is a biomaterial which found multiple applications in various branches. It is polysaccharide containing two types of polymers coexisting naturally: amylose and amylopectin, standing for linear and branched polymer form respectively. Both polymers are build using D-glucose monomers connected with α(1–4) glycosidic bond forming linear polymeric core of amylose and α(1–6) glycosidic bond introducing branching to amylopectin polymeric core [1].

Novel approach in polymer manufacture implies usage of composites e.g. polypropylene carbonate (PPC) are being doped with starch in order to create biofriendly, naturally degrading material, diminishing negative effect of polymeric waste production [2–4]. Starch is also showing very interesting optical properties. For example second harmonic light generation can be obtained on starch granules [5–7]. There have been designated $\chi^{(2)}$ tensor for starch granules confirming cylindrical symmetry of amylopectin [5,8]. Refractive index has been measured as $n = 1.515$ ($\lambda = 632.8$ nm) for starch acetate and for pure starch $n = 1.520$ [9,10]. As a material, starch can be fabricated having form of anisotropic transparent gels [11], but also it is possible to fabricate starch based nanostructures, as granules. It has been confirmed, that starch assist in formation of nanoparticles e.g. during gel assisted laser ablation, forming Ag nanoparticles [12–14]. All observed properties of this biomaterial allows it to be used in wide range of branches starting from food production through material engineering and optics, ending on nanoparticles fabrication as a crucial part of novel drug delivery systems [15].

It was previously confirmed that random lasing could be observed in systems based on biological matter like dye-doped biopolymeric matrices containing deoxyribonucleic acid (DNA) strands [16]. Moreover due to the low oxygen permeability properties we can expect improvement of photostability of starch based systems with respect to DNA based materials [17,18]. Such a design opens new possibilities in development of photonic materials based on biological matter. Costs and availability of matrices prepared from starch are encouraging and can be reduced to costs of fluorescent dyes used as dopants in biomaterials.

2. Experiment and experimental results

Biopolymeric matrix for random lasing applications has been prepared from starch doped well-known and characterized in details Rhodamine 6G (Rh6G) laser dye.

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Selection of this fluorescent dye was dictated with its properties, especially water solubility. Rh6G excitation spectra confirms possibility of excitation with Nd:YAG laser in doubled frequency $\lambda = 532$ nm.

High quality starch of 99% starch content in dry mass and 19.5% moisture extracted from potatoes was purchased from P.P.H. KROS. The material has been weighted, dispersed in water and heated up to about $T = 80$ °C, which corresponds to sol–gel transition temperature of starch from selected origin [19]. Above this temperature gelatinization occurs by cleavage of hydrogen bonds causing water to penetrate complex structure of starch resulting in increase of solubilization. Rh6G used as the fluorescent dye has been dissolved in water in appropriate amount and mixed with 1:1 volume ratio with starch solutions obtaining 1.0% (w/w) starch to water concentration and 1.0% (w/w) of Rh6G:starch weight ratio. Such prepared solution was deposited on glass slide with drop-casting method. Sample was left in ambient temperature, in air until solvent evaporated, forming a layer of starch doped with Rh6G.

In Fig. 1a we show the luminescence excitation and emission spectra from the 1% Rh6G:starch water solution carried out on Hitachi F-4500 spectrofluorometer. The Rh6G molecules can be excited with light of either of two wavelength ranges between 325 up to 375 nm and from 450 up to 550 nm. The fluorescence emission shown in Fig. 1a has been collected for $\lambda_{exc} = 350$ nm. Light amplification (amplified spontaneous emission – ASE) and random lasing in Rh6G doped starch matrix was measured in experimental system composed of Nd:YAG nanosecond laser (6 ns, 532 nm), mounted half-wave plate and polarizer responsible for precise change of pumping energy. Light of excitation wavelength ($\lambda = 532$ nm) results in nearly optimum excitation efficiency. The beam expander was used to form parallel beam followed by movable shutter and cylindrical lens. Such a designed optical system allowed forming stripe-like shape of excitation laser beam with dimensions equal to 7×1 mm with nearly uniform spatial intensity distribution. Sample was excited on the edge of surface and the emission signal was gathered perpendicular to the excited beam using Andor Shamrock SR-163 fiber spectrometer working at resolution $\Delta\lambda = 0.1$ nm. Acquisition time was equal to $\tau = 1$ ms and pumping laser frequency was set to $f = 10$ Hz therefore emission spectra were collected from one to another excitation laser pulse.

In Fig. 1b are shown spectra of Rh6G doped starch aqueous solution and layer excited with nanosecond laser. One can observe a characteristic narrowing of the fluorescence linewidth above the ASE threshold and typical separated narrow peaks appearing in gain region with random fashion, which is also characteristic for random lasing with weak localization feedback mechanism. Such typical for RL phenomenon behaviour can be understood in terms of positive feedback coming from spontaneously formed scattering area with high surface roughness and/or starch granules, what is schematically shown in Fig. 2, however the influence of Rh6G aggregates formation, which create complex strong scattering system cannot be neglected at all. Rh6G aggregates beside light scattering can explain strong red shift of stimulated emission observed for the solid sample (see Fig. 1b), due to the fact that in highly concentrated dyes solutions the process of Rh6G aggregation occurs with formation of J-type aggregates with weak emission at about $\lambda = 575$ nm. There are H-type aggregates too, which quench fluorescence signal and finally higher order aggregates with fluorescence maximum at $\lambda = 600$ nm [20,21].

Morphology of biopolymeric film obtained with presented method and roughness parameter for studied layer was characterized with Veeco Dimension V Atomic Force Microscopy, where imaging was conducted in tapping mode in order to characterize layer quality. Structures observed on the surface had their origin in sample drying. Extended time of drying water from layer surface, performed in room temperature, caused backward transition from gel to sol forming on the surface starch granules affecting the heterogeneity of the surface and caused roughening of the matrix, measured with Atomic Force Microscopy as presented in Fig. 3a. RMS Roughness defined as $R_q = \sqrt{\frac{1}{n}\sum_{i=1}^{n}|y_i - \bar{y}|^2}$, where $\bar{y}$ stands for average height, y_i stands for height in the following positions, was

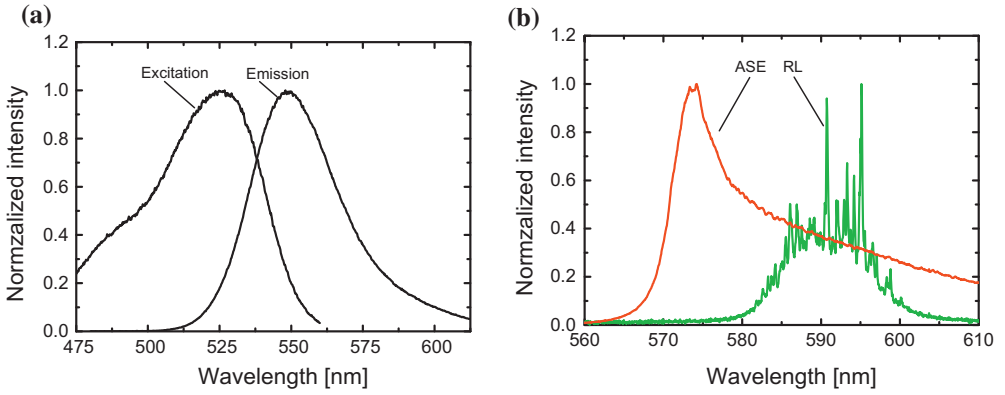

Fig. 1. (a) Fluorescence excitation, emission spectra of Rh6G in water solution and (b) amplified spontaneous emission (ASE) gathered from Rh6G:starch water solution and random lasing (RL) emission spectrum from Rh6G:starch biopolymeric matrix (in slab waveguide). Measurements conducted for pumping energy equal to $\rho = 126$ mJ/cm^2 and $\rho = 7.5$ mJ/cm^2 for ASE and RL respectively.

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