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Collagen network as the scaffold for spontaneously distributed optical resonators

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ABSTRACT

The idea behind this work was to acquire one dimensional lasing in the Rhodamine 6G dye doped collagen fibers with the control of random lasing phenomenon properties by changing the dye molecular arrangement. We show that a simple manipulation of the dye concentration in biopolymeric fibril matrix bulk and an additional use of α-cyclodextrin (α-CD) molecules determine formation of specific dye aggregates and as a consequence the shift of the random lasing emission wavelength in the desired direction. The analysis of the light transport mean free path in function of the dye and (α-CD) concentration was done with the use of coherent back scattering technique.

1. Introduction

Bioderived and bioinspired materials are of immense current interest because they can provide novel, attractive physical properties while being able to be produced by “green”, environment-friendly technologies. One of them is collagen, whose name originates from Greek *cola,* meaning glue [1]. Collagen is a chiral molecule with finds a growing interest for application in photonics. It is also one of the most spread proteins in human body which plays a role of scaffold for mammalian tissues providing them the elasticity and the durability. Structurally collagen is composed of three polypeptide chains forming α-helix, linked together by hydrogen bonds between hydroxylysine and hydroxyproline and by covalent bonds, that can form different collagen folding forms. Several examples of interesting photonic applications of collagen have been presented in the past. The building unit of collagen is the tropocollagen. It is a noncentrosymmetric molecule, exhibiting second harmonic generation (SHG) as observed by several research groups. The first observation of SHG in collagen was reported by Vasilenko et al. as early as in 1965 [2] what was confirmed later by Fine and Hansen as well as by Roth and Freund [3–5]. Yova et al. have shown the optical second harmonic generation by collagen Type I. A broad wavelength tuning of harmonic wavelength from 383 to 532 nm was achieved [6]. The same group presented also Rhodamine 6G (Rh6G) and collagen application for energy transfer, in which Rhodamine serves as a donor in the system after the excitation to S_2 energy level by 1064 nm via two photon absorption. Collagen, as an acceptor, has shown the fluorescence emission maximum intensity at 390 nm [7].

As a part of the light amplification system, collagen was used as an integral building block of a bone tissue, in which the random lasing phenomenon was observed, however the crucial role in this process was attributed to the hydroxyapatite, responsible for strong light scattering, in order to acquire spontaneously formed optical resonators [8]. Basing on this approach a method of morphology deformations detection, recording the changes in random lasing emission in bone during a stress applied to the tissue was developed [9]. The random lasing, was also observed in the egg membranes, enriched with Rhodamine 6G. Such a natural membrane, among the others, contains the collagen in its structure. Dense network of fibril proteins, positioned in random directions, are acting as scatterers for the optical cavities formation [10].

Cyclodextrins (CD) are circularly formed poly-glucose, playing a crucial role in the drug delivery as its carriers. The structure of cyclodextrin forms geometrical cone with hydrophobic interior and hydrophilic exterior [11]. Application of this material is driven by

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the formation of specific interactions inside the circular structure, capable to block diffusion of the compound from its interior. The mechanism standing for an efficient CD use, e.g. in drug delivery, is based on the cell membrane permeability for glucose moieties, reaching and penetrating them. The same happens with cyclodextrins, releasing their package of carried molecule inside the targeted cell. It was found that Rh6G and β-cyclodextrin are forming inclusion complexes (IC) having relation to the fluorescence emission wavelength and intensity from them [12,13]. However, the mentioned inclusion complexes are not revealing the detailed structure of Rh6G aggregates as it was done in the work of Martinez, concerning the laponite clay [14,15]. There have been accounted that formation of IC are responsible for the enhancement of fluorescence signal as presented for Rhodamine B and bis(cyclodextrin)s host [16].

In the present work we demonstrate that in the system based on fibril collagen proteins, serving role of a host material for fluorescent dyes and CD penetrating protein structure, lasing action can be achieved and due to the specific aggregates formation the emission wavelength can be easily shifted.

2. Materials and methods

For the light amplification studies we have selected the well-known water soluble Rhodamine 6G luminescent dye which possesses excellent fluorescence quantum yield. Collagen Type I, extracted from bovine derma, in gel form of concentration equal to 2.2%, was obtained from Collagen Department of Division Leather and Footwear Research Institute, Bucharest, Romania where the purification and the preparation procedure was performed according to the work of Albu [17].

Series of thin film samples were prepared by drop casting on glass slides. They were made using the gelatinized collagen with Rh6G concentration varying from 1% up to 3% (w/w) with respect to dry collagen. For one selected Rh6G:collagen ratio equal to 2% (w/w) additionally α-cyclodextrin purchased from Sigma Aldrich at molar ratios α-CD:Rh6G equal to 100:1, 10:1 and 1:1, respectively, was added. Quality and morphology of prepared thin layers were evaluated with the inverted optical microscope Olympus IX71 and atomic force microscope Dimension V (Veeco) in tapping mode.

The random lasing phenomenon studies were done using the experimental setup with pulsed nanosecond Nd:YAG laser, operating at $\lambda_{ex} = 532$ nm, as excitation source with stripe-like beam geometry of dimensions equal to 3.0×0.5 mm. Lasing spectra were collected by the Shamrock SR-163 fiber spectrometer in function of excitation energy density. Simultaneously to the random lasing emission measurements the optical visualization of the excited area was done using optical system of 0.8 μm resolution, capable to observe and correlate the emission to the position on the sample. Additionally to the light amplification experiments, the coherent backscattering (CBS) studies were performed, in order to get the value of light transport mean free path. It is a crucial parameter in analysis of the statistics of the distance that light travels before it is scattered.

3. Results and discussion

3.1. Collagen layers morphology

The microscopic studies show that dye doped collagen deposited on the glass slide is forming fibers arranged in random directions at the 2D surface area. The image analysis done with the ImageJ confirms this situation which results from the isotropic distribution of fibrous structures (Fig. 1a) [18]. The dye doped collagen thin films morphology study was performed by the AFM analysis. The acquired topographies, presented in Fig. 1b and d) indicate that the superhelix collagen fiber of diameter about $D_{fiber} = 5$ μm is formed and built from random coil macromolecules with diameter less than $d_{coil} < 50$ nm. The formed collagen loose protein network on the glass surface, surrounded with not fibrillated protein film containing Rh6G, and Rh6G aggregates in the fiber structure is shown in Fig. 1. All studied samples exhibit similar morphologic properties.

Dye free samples, as well as Rh6G doped collagen fibers casted on the glass slide were investigated using experimental system for CBS measurements. As a source of scattered light *cw* He–Ne laser of 633 nm emission wavelength was used, which is off the absorption of the samples. Incorporation of Rh6G and α-CD do not show significant effect to the calculated light transport mean free path therefore the designated parameters were evaluated statistically indicating the source of scattering overall the fiber network. The light transport mean free path was calculated for all samples using Equation (1) [19–21]. The obtained average value was equal to $l_t = 16.8 \pm 1.8$ μm meaning that this property is one of the whole system and not only for the single collagen fiber. Fig. 2 presents, as an example, the coherent backscattering cone for 3% (w/w) Rh6G doped collagen sample.

$$l_t = \frac{0.7 \cdot \lambda}{2\pi \cdot W} \tag{1}$$

where l_t is light mean transport path, $\lambda = 633$ nm, and W stands for the full scattering cone width at its half maximum.

3.2. Multimode fiber lasing

Collagen fibril proteins, enriched with Rh6G, become to be the light amplifying medium, able to exhibit the phenomenon of amplified spontaneous emission (ASE) and random lasing (RL). We have focused on the lasing action generation based on the distributed 2D network of dye doped collagen fibers. According to the known phenomenon, that we had described previously, we have used random fibril system in order to acquire tunable light emission relaying on formation of Rh6G aggregates sizing effect responsible for the shift of the light emission wavelength [22].

As was expected, the Rh6G aggregation affects to the RL emission properties. In the measured samples an RL tuning from 598 nm to the 610 nm with about ~10 nm spectral FWHM was observed, as presented in Fig. 3. This effect is related to the formation of J-aggregates and higher order aggregates responsible for the red shift of the emission wavelength [14,15]. The lasing modes were not clearly visible, due to the non-resonant feedback meaning the light intensity increasing in the gain medium upon excitation at the gain length [23–25]. With the microscopy analysis done during the lasing it was revealed that Rh6G forms inclusions, which are colocalized with the fibers positions and are acting as scattering centers embedded in the fiber structure as it is shown in Fig. 4.

Although Rh6G aggregates are playing the role of scatterers, the formation of resonant modes has not been observed and light is not localized within the inclusions in collagen fibers. Rather than the densely packed 2D fiber network is responsible for amplification with wave energy dissipation with scattering. Changing the pumping beam energy density a simultaneous “blinking”, coming from inclusions along the fibers, was observed. It is accounted as due to the reaching population inversion in the gain region responsible for the “on” and “off”, turning characteristic for random lasing presented in Fig. 4. Loading collagen fibers with increasing amount of Rh6G resulted in lowering the lasing threshold from $\rho_{1\%} = 6.0$ mJ/cm^2 for lowest Rh6G concentration (1% w/w), down to $\rho_{3\%} = 3.4$ mJ/cm^2 for 3% (w/w). This effect is related to the