Lasing from Organic Dye Molecules Embedded in Transparent Wood

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The report on a study of laser emission from a conceptually new organic material based on transparent wood (TW) with embedded dye Rhodamine 6G molecules is presented in this paper. The lasing performance is compared to a reference organic material containing dye in a poly-methyl-methacrylate matrix. From experimental results, one can conclude that the optical feedback in dye-TW material is realized within cellulose fibers, which play the role of tiny optical resonators. Therefore, the output emission is a collective contribution of individual resonators. Due to this fact, as well as low Q-factor of the resonators/fibers and their length variation, the spectral line of laser emission is broadened up to several nanometers.

1. Introduction

Recent advances in photonics, on both fundamental and engineering aspects, provide new opportunities for expansion of this field into numerous applications and technologies. The focus of the scientific interest is mostly directed toward the development of novel components and materials to realize featured functionality of the photonics. One of the most considerable efforts in this direction is the engineering of novel gain materials and design solutions for laser sources. In the past few decades, conceptually new types of lasers aiming different applications were introduced. For example, vertical-cavity surface-emitting lasers, noncavity scattering feedback lasers, so-called “random lasers,” lasers implementing surface plasmon polariton resonances—SPASERs, fiber lasers, lasers based on Raman or Brillouin scattering, etc.[1–12]

In this report, we demonstrate lasing action from a novel gain material containing organic dye Rhodamine 6G (Rh6G) embedded into transparent wood (TW) matrix. Besides the unusual origin and appearance of the investigated material, it has numerous advantages defined by the properties of components used for its fabrication. Organic dyes are of special interest as active media due to their broad-bend emission/absorption spectra and very high optical gain.[13–15] Transparent wood features light weight, modification accessibility, excellent mechanical performance, and structural anisotropy introduced by aligned hollow cells.[16,17] Optical transparency of TW is the most unique property, which extends its applications in various fields, including biosciences, lighting, building industry, and others.[17–19] Although this material (TW) is relatively new, it has already been tested for potential applications in optics, but so far only for implementation in passive photonic components.[18] However, due to its compatibility with polymer technology, TW is an interesting alternative for applications requiring optical activity, first of all lasing, where demanded materials should be inexpensive, easily handled and disposable.

2. Material Preparation and Characterization

As the TW itself does not possess any optical gain, a host matrix should be “activated” with an additional optically active medium, Rh6G dye in our case. The samples with dye embedded into TW structure were prepared in three technological steps (Figure 1). At the first step, balsa wood (Ochroma pyramidale, purchased from Wentzels Co. Ltd, Sweden) of thickness of 1.0 mm and 3.0 mm was deignedified using 1 wt% of sodium chloride (NaClO2, Sigma-Aldrich) in acetate buffer solution (pH 4.6) at 80 °C, until the wood was totally bleached. Then the deignedified wood was dehydrated with ethanol and acetone, sequentially; each procedure was repeated three times. At the second step, wood template was put in dye (Rh6G 99%, SIGMA-ALDRICH) aceton solution with a concentration of 1 × 10⁻³ mole/L. Finally, the wood template was fully infiltrated into the pre-polymerized MMA solution and then cured at 75 °C for 4 h.

The surface and cross-sections of the TW samples were investigated with a field-emission scanning electron microscope (Hitachi S-4000, Japan) operating at an acceleration voltage of 1 kV. The samples were roughly polished and coated with Pt/Pd before SEM imaging. The length of fibers constituting the wood material varies in range of 200–1000 μm, whereas the lumen
(pore) size falls in 10–70 µm range (Figure 2a,b). The fibers of larger size, vessels, seen on the microscope picture under white light illumination, have lumen size of the order of hundreds of micrometers (Figure 2c). After dye loading and poly-methyl-methacrylate matrix (PMMA) infiltration, the wood attains red color associated with the presence of Rh6G (Figure 2d, inset). High optical transmittance of TW (Figure 2d, blue curve, corresponding to the sample shown in Figure 2c), was modified by dye absorption leading to a rapid drop of the transmission at corresponding wavelengths (Figure 2d, red curve). The transmittance measurements were performed in an integrating sphere with the use of a broadband light source (EQ-99 from Energetiq Technology, Inc.). The wood matrix not only makes the material unique but also improves its mechanical properties in comparison with the reference sample without wood matrix (dye-PMMA) due to the wood tissue reinforcement of PMMA.\(^{[17]}\)

One needs to notice that mechanical properties of TW-dye composite do not modified by the dye (Rh6G) since its mass concentration is small in comparison to the wood density and the hydroxyl groups on wood substrate, mainly contributing to composite mechanical properties, are not influenced by dye.\(^{[20]}\)

A reference material, Rh6G in PMMA host matrix, was used in our investigations to compare and justify specific features of the lasing performance achieved in TW-dye medium. The methods of fabrication and characterization of the reference material are given elsewhere, since the technology is established and well-known.\(^{[21]}\)

The concentration of dye (Rh6G) before polymerization was chosen to be the same (1 × 10\(^{-3}\) mole/L) in both TW-dye and PMMA-dye materials. In our case, a classical external resonator is absent, and, therefore, optical losses in the system are expectedly high. To obtain laser action, the optical amplification, mainly defined by the concentration of dye molecules (Rh6G), should overcome the losses. Therefore, the high concentration of dye is desirable. On the other hand, the upper limit of the dye concentration (typically 5–10 × 10\(^{-3}\) mole/L) is set by the formation of dye dimers which can cause the quenching of dye luminescence.\(^{[13,15]}\) Considering the facts mentioned above the concentration of Rh6G was chosen to be 1 × 10\(^{-3}\) mole/L.

### 3. Experimental Set-Up

In this study, the authors used a transversal pump geometry justified by the short absorption depth of the pump light (200–300 µm) in the dye material, and the need of achieving a large illuminated volume.\(^{[13,15]}\) The authors implemented the scheme from the variable stripe length (VSL) method typically applied in gain estimation experiments (Figure 3).\(^{[22,23]}\) The frequency-doubled output (\(\lambda = 532\) nm) of a Q-switched Nd:YAG laser (Quantel Brio) with the pump repetition rate of
5 Hz, pulse duration of 4 ns, and pulse energy of 7.5 mJ was focused with a cylindrical lens on a sample surface into a line of 200 µm width. The TW sample embedded with Rh6G dye exhibits anisotropic scattering properties specified by its fiber-based nature. Therefore, the optical excitation of the material was realized in a preferable direction, i.e., the pump line was located along the cellulose fibers in the longitudinal direction.

In order to reduce the influence from pump intensity gradient (for example, thermal lensing), uniform intensity distribution along a pump line was achieved by expanding a Gaussian beam and selecting its central part with a square diaphragm before focusing. The investigated samples had a rectangular shape with the 9–10 mm length along the pump line. Fluorescence was collected with a 400 µm-core multi-mode fiber (MM fiber) from the sample facet perpendicular to the pumping direction, and analyzed with a spectrometer (Acton, SpectraPro 2500i, Princeton Instruments) based on CCD matrix (Roper Scientific, 7346–0005, Princeton Instruments) cooled down to −100 °C. The single shot spectrum acquisition was triggered by an electrical signal from the laser synchronization port.

4. Lasing from the Dye Embedded Transparent Wood

Although a classical resonator with external mirrors was not used in our experiments, the TW matrix impregnated with dye demonstrated laser radiation under proper pumping conditions. To analyze the laser action from the material, we run two series of experiments investigating the dependence of the lasing output (1) from pump power at constant pump line length and (2) from pump line length under constant pump intensity. Parameters of the TW-dye laser were evaluated from experimental data obtained in measurements described below.

For the first series of optical measurements, pump energy was varied with neutral density filters from 0.8 to 6 mJ (Figure 4a). The spectral width of the output signal was several nanometers which is a reasonable indication of laser action, considering the typical luminescence linewidth of Rh6G ≈ 30 nm. As one can see from Figure 4a, a fine spectral mode structure is resolved on the top of each spectral line. This measured mode pattern remains stable for different excitation energy; that is another relevant indication of the lasing. We assume that separate cellulose fibers can work as tiny resonators with the feedback mechanism provided by scattering inside the composite...
structure. Consequently, the output spectrum line (≈5–6 nm full width at half maximum FWHM) is a superposition of the lasing modes from individual fibers/resonators of different lengths and diameters. The prominent peaks at the top region of a spectrum are contributions from the resonators with the preferable lasing conditions. Also one needs to notice, that ASE produced by a substantial amount of the resonators which did not achieve lasing threshold conditions, is also detected in our experiment. It is observed as broadening of the spectral wings at the bottom of each spectrum (Figure 4).

In the second series of measurement, we analyzed the behavior of radiation spectrum by variation of the pump line length. The length controlled by a shield determines the amount of active resonators within the excited volume (Figure 3). The contribution of separate resonators can be seen as a fine spectral pattern (Figure 4b) at the pump line length comparable to the length of cellulose fibers (0.2–1 mm). The elongation of the pump line causes the activation of more individual resonators/fibers contributing to the lasing (equivalent to the averaging over an ensemble of a large amount of independent events in statistics). Their contribution at longer pump line results in blurring the overall spectrum and, as a consequence, the width of the emission peak is broadened up to 6 nm. It is worth to notice, that the diameter of separate fibers (10–70 µm) is not a critical issue for lasing performance. This means that emission spectra will keep similar shape for samples of different widths as long as they are larger than the penetration depth of pump light (200–300 µm).

The stability of the spectral pattern from pulse to pulse under optical pumping indicates cavity optical feedback (Figure 4c). It is a significant result because in the case of varying spectral pattern it would indicate inhomogeneous scattering inside the material and random lasing (RL).[3–6]

An important laser parameter is the dependence of the output from the pump pulse energy (laser curve). It has to be noted that this characteristic is individual for a laser, i.e., it depends on the properties of the resonator as well as pumping conditions. In our experiment we were able to vary the number of active resonators via pump line length. Therefore, the dependence on the Figure 5 is the specific one for the used pumping parameters (pump line length was 3.25 mm). To obtain the laser curve we recalculated laser output energy by integrating the intensity (measured in photon counts by spectrum analyzer) over spectral bandwidth and multiplying its value by a proper conversion (counts-to-mJ) coefficient. The slope efficiency of TW-dye laser for the specific pump conditions was 11% with the threshold pump energy equal to 0.7 mJ.

5. Comparative Analysis of the Lasing Mechanism in TW-Dye Structure

To reveal the impact of cellulose fiber structure of the TW-dye medium on the lasing features, we compare the results discussed in the previous section to the ones obtained with Rh6G-PMMA material under the same experimental conditions. Similarly to the case of TW-dye structure, the evolution of the output signal spectrum with increased pump pulse energy as well as pump line length demonstrates gradual transition from photoluminescence to amplified spontaneous emission (ASE). At the same time, narrow peaks of stimulated emission are clearly seen on the top of the radiation spectrum (Figure 6). As in the previous case, the stable mode pattern with an increase of pump pulse energy indicates the laser action (cf. Figure 4a and Figure 6a). However, in comparison to the case of TW-dye material, more peaks appeared with the elongation of the pump
line, whereas the position and the separation between the existing peaks remained constant (Figure 6b). These narrow peaks can be attributed to separate lasing modes originating from a laser cavity.

It is important to note that spectral peaks corresponding to separate modes in the PMMA-Rh6G sample become stronger and more distinguishable upon increasing the pump line length (Figure 6b), whereas TW-Rh6G sample demonstrated an opposite trend, i.e., mode peaks are blurred out with the pump line length increased (Figure 4b). With a reasonable assumption, the PMMA-Rh6G sample facets can form a Fabry–Perot resonator. It is well known that light experiences reflection at any interface between media of different refractive index. In our case, the reflection coefficient for PMMA, estimated from Fresnel equation is 4%–5% (for normal incidence) which ensures formation of a low Q-factor resonator.\(^{[25]}\) Refractive index of PMMA in the visible range is about \(n = 1.5\) which is enough to build up such a resonator, where high losses due to low reflection of the facets are compensated by high quantum yield of Rh6G (0.99, from the supplier). Stability of the mode pattern, as well as peak separation, with elongation of the pump line, justify that the geometry of the resonator was not changed. Since there are no other possible feedback mechanisms involved, for example, scattering as in the case of RL, one can conclude that the facets of the sample formed an optical resonator. The narrowing of the luminescence linewidth down to \(10 \text{ nm}\) indicates the laser action as well (Figure 6b, inset). Low quality of the Fabry–Perot cavity results in overlapping of numerous competing modes and, as a consequence, broad linewidth, where only limited amount of separate mode lines can be spectrally resolved. Stability of the mode structure, or spectral peak pattern, with numerous experimental realizations (repeated pumping shots) (Figure 6c) is an additional argument to exclude any other reasons for the cavity formation, but Fabry–Perot bulk resonator.

In order to highlight the difference of the optical feedback origin in TW-dye and PMMA-dye materials, it is essential to analyze the behavior of the spectral linewidth with a pump line length in more details (Figure 7). The TW-dye sample demonstrated rapid decrease of the FWHM with the increase of pump line length (Figure 7a) which finally approached constant value (FWHM = 5 nm). As one can see, transition from fluorescence to laser emission occurs as soon as the pump line reaches the value (≈1 mm) comparable to the fiber/resonator length (0.2–1 mm). In contrast to the TW-dye laser, the spectral line of the reference material (dye-PMMA) was narrowed gradually with the pump line length and reached minimum of FWHM (10 nm) at almost twice longer length of the pump line (Figure 7b). The reason for such a difference in the FWHM behavior is the realization of the optical feedback: many small fibers/resonators (TW-dye) or bulk cavity formed by facets (Rh6G-PMMA). The resonators in TW-dye were formed as soon as the pump line was long enough to fully illuminate cellulose fibers. The laser emission in the Rh6G-PMMA was observed when amplification of the pumped region overcame loses in the resonator.

Summarizing the experimental sections above, it worth to mention that the main reason of the difference in optical feedback mechanism for two materials under investigation is caused by different structure of both gain media, that is reflected in the amount of optical resonators contributing to the lasing. Our experimental results show that the feedback mechanism in TW-dye material is realized by cellulose fibers which act as a large ensemble of tiny resonators. Consequently, the emission spectrum of TW-dye PMMA is the result of collective contribution of these resonators as well as ASE inevitably collected during the measurements. In the reference sample (Rh6G-PMMA), the facets form only one large Fabry–Perot resonator with the dimensions determined by the sample length.

6. Summary

In this paper we present the possibility of integration of an organic dye, for example, Rh6G, within the TW matrix. Such material possesses specific optical and mechanical properties. Most interestingly, it shows lasing action under favorable pumping conditions, in particular, transversal pump geometry. Comparative analysis of the experimental results for the TW-dye material and the reference medium (PMMA-Rh6G) implies that cellulose fibers operate as small optical resonators. The emission spectrum in such material (TW-dye) is the result of the superposition of lasing modes produced by individual resonators. Collective contribution of fiber-based resonators as well as their size variation causes the broadening of the emission line up to several nanometers. The technology discussed in this report can have large potential for implementation in different optical applications, e.g., biophysics, environmentally friendly and sustainable illumination, as well as in wood material studies.

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