Doctoral Thesis in Physics

Light propagation and photonic functionalization of semi-ordered material (transparent wood)

ADIL BAITENOV

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Abstract

Investigating novel materials requires understanding their chemical and optical properties, which allows for finding their uses through functionalization by chemical modification. In this thesis, we are focusing on a material with high anisotropic scattering - transparent wood. This biocomposite material has a hierarchical structure ranging from nanometer to hundreds of micrometers scale, and natural ordering, which is between perfectly ordered and fully random structure. Optical transparency in the visible range and the unique structure of transparent woods show good potential for functionalization.

Due to complex structure and nonhomogenous chemical composition, not all characterization methods are fitting. While relatively straightforward properties like transmittance and haze can be measured using known techniques, but additional investigation was required to understand light behavior and measure other properties. In this work, the modeling method for investigation of light propagation and estimation of the effective refractive index of transparent wood for a deeper understanding of a material.

Transparent wood has shown excellent host properties, capable of holding high concentrations of Rhodamine 6G laser dye without aggregate formation. In this dissertation, we present the analysis of the host properties of transparent wood and show that the dye forms statistical energy traps at high concentrations of dye.

By doping transparent wood with active dye and pumping it with SHG Nd:YAG green laser, the optical gain within the active media can be achieved. The feedback in this optical system is occurring via scattering on fiber walls, showing behavior similar to random lasers. However, due to the semi-ordered structure and wave-guiding effect of transparent wood, the transparent wood laser is referred to as a "quasi-random laser". The lasing emission can be further enhanced by the introduction of an external cavity, virtually expanding the active media allowing more lasing modes to be resolved, and increasing laser power.

This work demonstrates the characterization of transparent wood optical and chemical properties and develops a computational model that can be used for further investigation of light behavior in semi-ordered anisotropic media.
The functionalization of transparent wood is demonstrated by the introduction of a quasi-random laser and modification of that laser is presented.

**Keywords:**
light scattering, scattering material, hierarchical structure, FEM model, wood modification, random lasers, dye lasers, transparent wood, adsorption, diffusive media.
Sammanfattning


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List of appended papers

Paper A
Hui Chen, Adil Baitenov, Yuanyuan Li, Elena Vasileva, Sergei Popov, Ilya Sychugov, Max Yan and Lars Berglund "Thickness Dependence of Optical Transmittance of Transparent Wood: Chemical Modification Effects". ACS Applied Materials and Interfaces. 2019

Paper B
Elena Vasileva, Adil Baitenov, Yuanyuan Li, Ilya Sychugov, Max Yan, Lars Berglund and Sergei Popov "Effect of transparent wood on the polarization degree of light". Optics Letters. 2019

Paper C

Paper D
Martin Höglund, Adil Baitenov, Lars A. Berglund, Sergei Popov "Transparent wood biocomposite of increased, well-dispersed dye content for fluorescent and lasing applications". Advanced Optical Materials. 2023

Paper E
Adil Baitenov, Ravi Shanker, Martin Hoglund, Lars Berglund, Sergei Popov "Emission enhancement of coupled microcavity wood laser through external cavity". Manuscript

Paper F
Martin Höglund, Adil Baitenov, Lars A. Berglund, Sergei Popov "Improved spectral brightness by tailored optical scattering in dye doped transparent wood biocomposites for fluorescent and laser applications". Manuscript
Division of work between authors

Paper A

Second Author - Participated in part of planning; Participated in performing the optical measurements work and wrote part of the manuscript.

Paper B

Joint First Author - Major contribution to planning; Performed all experimental work, contributed to model development and manuscript.

Paper C

Second Author - Contribution to planning; Participated in performing the optical measurements work, data analysis and writing of the manuscript.

Paper D

Joint First Author - Major contribution to planning; Performed all laser setup work and lifetime decay measurements, contributed to manuscript writing.

Paper E

Joint First Author - Major contribution to planning; Performed all laser setup work, data analysis and manuscript writing.

Paper F

Second Author - Participated in part of planning; Participated in performing the optical measurements work and wrote part of the manuscript.
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Nomenclature

\( \lambda \)  Wavelength
\( \mu \)  Permeability
\( \omega \)  Angular velocity
\( \varepsilon \)  Permittivity

\textit{ASTM}  American Society for Testing and Materials
\( c \)  Speed of light
\textit{CCD}  Charge-coupled device
\textit{COMSOL}  COMSOL Multiphysics software
\( DOP \)  Degree of polarization
\textit{FEM}  Finite element method
\( FWHM \)  Full-width at half maximum
\( IR \)  Infrared
\( LP \)  Linear polarizer
\textit{MC}  Monte-Carlo
\textit{PMMA}  Polymethyl methacrylate
\( QWP \)  Quarter wave plate
\( QY \)  Quantum yield
\textit{Rh6G}  Rhodamine 6G
\( RI, n \)  Refractive index
NOMENCLATURE

$SEM$ Scanning electron microscope

$SHG$ Second harmonic generation

$TMFP$ Transport mean free path

$TW$ Transparent Wood

$V_p$ Phase velocity
Chapter 1

Introduction

This chapter overviews the research. It provides goals, research and an outline of this work.

1.1 Background

Optics is the fundamental science that studies the properties of light, how it interacts with matter, and instruments used for the detection and measurement of optical phenomena [1]. There is an extended research work on light interaction with ordered and random media [2–8], but not on semi-ordered materials, such as transparent wood (TW), which is the focus of this dissertation.

Transparent wood is a novel material, produced by chemical modification of natural wood [9–18]. The initial sample goes through the process of delignification, which uses NaClO solution to lower lignin content, followed by filling it with refractive index matching polymers like methyl methacrylate or thiolene. The TW is characterized using transparency (up to 90% for 1 mm thickness) and haze measured with integrating sphere [12, 13, 19].

One of the unique properties of TW is that it conserves the hierarchical structure of native wood, which consists of components of varying diameters – fibrils, fibers, wood rays and vessels [20–22]. This unique structure is the source of anisotropic scattering and mechanical strength in TW, creating hazy (highly scattering) material with a high number of fibers that can act as hosts for active materials, e.g. laser dyes [23, 24].

In order to investigate light interaction with matter in TW and to improve its transmittance and lower haze, one needs to choose the polymer with the closest refractive index. That can be achieved experimentally, by preparation of a set of polymers with different refractive indices, or analytically [17, 25]. However, even though transparent wood is consisting mostly of cellulose refractive index of which was measured before, it also consists of residual lignin and other ma-
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Materials. That makes the analytical approach of calculating the refractive index to find the proper polymer challenging and as time-consuming as the experimental approach. Another method that was used to find a matching polymer is the computational approach, by creating a computational model based on wood geometry in COMSOL and comparing its output for ray distribution with experiments.

Material functionalization is the process of adding new functions or properties to a material by chemical change of material or by embedding of other materials [26]. One can take advantage of natural material properties, such as high scattering and anisotropcity, to tailor material for specific use. Modification of transparent wood by impregnation with Rhodamine 6G active dye allows to achieve lasing, where optically active dye in conjunction with high scattering leads to optical gain and lasing [27][28].

In conventional lasers, optical gain is achieved through reflection within an external resonator, which usually consists of a full and partial mirror, and it is a very ordered, highly researched system [29]. On the other side of the spectrum, in random lasers optical feedback occurs within media with randomly distributed scattering centers with no external cavity [30–37]. Transparent wood laser, due to its hierarchical, anisotropic structure, is lying within the two types of lasers. Based on previous research, it was concluded that separate fibers of TW laser are acting as separate lasers, creating the output of high brightness and low coherence [38]. Additionally, the fiber and vessel structures of wood create a wave-guiding effect, partially increasing the amount of laser emission along the fibers [27]. Because of these features we classify the TW laser as a quasi-random laser. Additionally, the modification of the TW quasi-random laser with an external mirror to amplify the emission is investigated in this dissertation.

1.2 Research goals

This dissertation summarizes the research on light propagation in transparent wood (TW). One of the unique properties of that material is the hierarchical structure, which is conserved in process of sample preparation from native wood. That structure is neither ordered nor random, opening high potential with its wave-guiding effect of fibers and ability to use it as a host for functionalization. In order to investigate TW, its properties and how it can be functionalized, the following goals are set:

- Analysis of optical properties of TW based on sample thickness, wood species and input light polarization
- Characterization of TW properties and light interaction
- Development of computational model based on wood structure geometry
• Investigation of TW in the role of a host for laser dye
• Demonstration of quasi-random laser based on TW and its improvement

For functionalization, TW samples were impregnated with laser dye (Rhodamine 6G), and its emission was analyzed at different pumping and concentrations of dye. The effectiveness of TW as a host for optic dyes in comparison to other materials was investigated. The improvement of emission properties and increase in the number of resolved modes in TW laser with the addition of an external mirror were demonstrated.

1.3 Outline

Chapter 1 presented the research goals and steps taken to reach the aforementioned goals. It is followed by Chapter 2, which focuses on the fundamentals of light behavior and material properties that affect light propagation, focusing on scattering.

Chapter 3 describes the background of TW, its use as functionalized material, and the simulation of light propagation in TW. It starts with a description of the TW structure and preparation process of samples. It is followed by the characterization of the material and functionalization of TW by impregnation with optically active dye (Rh6G) and analysis of TW's qualities as a host.

Chapter 4 presents the fundamentals of random lasers as well as TW-based quasi-random laser. The laser emission of TW can be improved by the introduction of an external mirror, which improves the lasing and increases the number of resolved modes in the TW laser. The waveguiding effect of wood structures further improves the effect of the external mirror and output of the quasi-random laser.

Chapter 5 summarizes obtained results and possible future work on these topics.
Chapter 2

Fundamentals of light

This chapter gives theoretical background on the properties of light and the modeling of its behavior. The chapter starts with the introduction of Maxwell’s equations to discuss the main properties of light waves. It is followed by a discussion of light behavior in materials and how it can be used to characterize transparent wood.

2.1 Fundamentals of light

Light is electromagnetic radiation that can be detected with the human eye, with visible light lying within 400 to 700 nm with different wavelengths corresponding to different colors observed. Physical properties of light can be derived from its wave-particle duality, which means that it follows both wave and particle-like behaviors. Due to duality, light has the properties of the wave, such as spectrum, coherence, polarization, amplitude and frequency and properties of the particle, like photon energy, spin and momentum. That also means that some observed light phenomena that can be explained only in terms of particles (photoelectric effect, entanglement states) or waves (interference, diffraction, coherence and polarization) [29].

In 1816 Fresnel and Arago have shown that light is a transverse electromagnetic wave, and derived Fresnel-Arago laws, that describe interference for different cases [39]. Like any electromagnetic wave, light can be described with Maxwell Equation in Oliver Heaviside and Willard Gibbs vector notation:

\[ \nabla \cdot \vec{E} = \frac{\rho}{\varepsilon}, \]  
\[ \nabla \cdot \vec{B} = 0, \]  
\[ \nabla \times \vec{E} = \frac{\partial \vec{B}}{\partial t}, \]
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\[ \nabla \times \overrightarrow{B} = \mu \overrightarrow{J} + \mu \varepsilon \frac{\partial \overrightarrow{E}}{\partial t}, \tag{2.4} \]

where \( \overrightarrow{E} \) and \( \overrightarrow{B} \) are electric and magnetic field vectors, \( t \) is time, \( \mu \) and \( \varepsilon \) are permeability and permittivity of the media \( \rho \) is electric charge density and \( \overrightarrow{J} \) is a displacement current.

The first two equations (2.1 - 2.2) are corresponding to Gauss law for electric and magnetic fields respectively, stating that the electric flux of any enclosed surface is proportional to the total charge enclosed within the surface, and the net magnetic flux out of any closed surface is always equal to zero, which means the impossibility of the existence of magnetic monopole. The third equation is Faraday’s law of induction (2.3), stating that time and/or spatially varying electric field always accompanies a time-varying magnetic field. The fourth equation is Ampere’s law, which shows that in the case of the static electric field, the spatially-varying magnetic field is proportional to the temporally-varying electric current and vice versa [29].

Often, in optics, there are no free charges or currents, so in most cases \( \rho \) and \( \overrightarrow{J} \) are equal to zero. Based on that, eq. 2.3 can be rewritten as a wave equation for an electric field propagating in free space:

\[ \frac{\partial^2 \overrightarrow{E}(\overrightarrow{r}, t)}{\partial^2 t} = c^2 \nabla^2 \overrightarrow{E}(\overrightarrow{r}, t), \tag{2.5} \]

where \( \nabla^2 \) is the vector Laplacian and \( c \) is the speed of light in vacuum, which can be represented as \( c = 1/\sqrt{\mu_0 \varepsilon_0} \). Solution of eq. 2.5 is a plane wave written as:

\[ \overrightarrow{E} = \overrightarrow{E}_0 \cos(\overrightarrow{k} \cdot \overrightarrow{r} - \omega t + \varphi), \tag{2.6} \]

where \( \overrightarrow{E}_0 \) is the amplitude of the electric field, \( \overrightarrow{k} \) is wave vector, \( \omega \) is the angular velocity and \( \varphi \) is initial phase. Vectors \( \overrightarrow{E}, \overrightarrow{B}, \) and \( \overrightarrow{k} \) form an orthogonal triad following the right-hand rule.

The speed of light propagation through material is called group velocity and can be described with:

\[ v_p = c/n, \tag{2.7} \]

where \( v_p \) is phase velocity, \( c \) is the speed of light in vacuum and \( n \) is refractive index.

Refractive index dependency on frequency does not derive directly from Maxwell’s equations, but it can be observed experimentally. In order to explain the dependency, we need to apply the model of a forced oscillator from classical mechanics. Atom can be considered a simple oscillator with a resonant frequency of \( \omega_0 \). When an electrical field is interacting with a material, electron positions are shifted relative to a positively charged nucleus forming a dipole and inducing an electric dipole moment. The charge are oscillating with changes
of the electric field in time, re-emitting light of the same frequency, which is described as elastic scattering. In cases when the frequency of light matches the resonant frequency, an atom or a molecule absorbs the light and reaches an excited state. Then, through spontaneous emission atom or molecule return to the ground state by emitting a photon \[29\].

Light incident on a material affects charge \(q_e\) with a driving force \(F_e\) proportional to the electric field \(E(t)\):

\[
F_e = q_e E(t) = q_e E_0 \cos \omega t. \tag{2.8}
\]

Opposite to the driving force, the restoring force is applied to return the system to equilibrium. By applying Newton’s Second Law we derive the equation of motion, the sum of forces equal to the mass times the acceleration:

\[
q_e E_0 \cos \omega t - m_e \omega_0^2 x = m_e \frac{d^2 x}{dt^2}. \tag{2.9}
\]

To satisfy that expression, \(x\) has to be a function whose second derivative isn’t very different from \(x\) itself. Since electron oscillates at the same frequency as \(E(t)\), the solution can be written as:

\[
x(t) = x_0 \cos \omega t, \tag{2.10}
\]

and by substituting it in the equation we can find that:

\[
x(t) = \frac{q_e/m_e}{(\omega_0^2 - \omega^2)} E(t). \tag{2.11}
\]

This is the relative displacement between the negative cloud electron and the positive nucleus.

The dipole moment is equal to the charge \(q_e\) times its displacement, and for \(N\) contributing electrons the density of dipole moments takes the following form:

\[
P = q_e x N = (\varepsilon - \varepsilon_0) E(t) = \frac{q_e^2 NE}{m_e} \frac{E(t)}{(\omega_0^2 - \omega^2)}, \tag{2.12}
\]

which when solved for \(\varepsilon\) takes form of:

\[
\varepsilon = \varepsilon_0 + \frac{P(t)}{E(t)} = \varepsilon_0 + \frac{q_e^2 N/m_e}{(\omega_0^2 - \omega^2)}. \tag{2.13}
\]

Using the fact that \(n^2 = \varepsilon/\varepsilon_0\), we can derive the expression for \(n\) as a function of \(\omega\), known as a dispersion equation:

\[
n^2(\omega) = 1 + \frac{N q_e^2}{\varepsilon_0 m_e} \left( \frac{1}{\omega_0^2 - \omega^2} \right). \tag{2.14}
\]
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In the case of dielectrics, there are atomic, ionic and orientational polarizations. Due to lower inertia in comparison to molecules, atoms’ contribution is more significant at higher frequencies. Thus, the refractive index is based on the interaction of electric polarization mechanisms with different weight factors \( f_j \) contributing at different frequencies of the incident light. Due to losses during light transmission, the imaginary part of the refractive index indicates the attenuation of the signal. Thus, the final form of eq. (2.14) becomes:

\[
 n^2(\omega) = 1 + \frac{N q_e^2}{\varepsilon_0 m_e} \sum_j \frac{f_j}{\omega_0^2_j - \omega^2 + i \gamma_j \omega} = n_0(\omega) + k_0(\omega)i,
\]  

(2.15)

where \( n_0 \) is the real part, the refractive index value that indicates the change in phase velocity, \( \gamma_j \) is the damping coefficient and \( k_0 \) is the extinction coefficient, responsible for absorption and scattering of light in a material. Thus, it can be concluded that the refractive index changes depending on the frequency of the incident light [29].

![Refractive index of cellulose vs wavelength](image)

Figure 2.1: Refractive index of cellulose \((C_6H_{10}O_5)_n\) dependence on wavelength

Based on previous empirical observations of the refractive index dependence on frequency Sellmeier equation of dispersion was proposed in 1872:

\[
 n(\lambda) = \sqrt{1 + \sum_j \frac{A_j \lambda^2}{\lambda^2 - B_j^2}},
\]  

(2.16)

where \( \lambda \) is wavelength, and \( A \) and \( B \) are coefficients that are usually obtained with least-square fitting as seen in fig. 2.1 [29].
Propagating electromagnetic waves consist of oscillating electric and magnetic fields which are always perpendicular to each other. The property that describes the orientation of an oscillating electric field is called polarization, and depending on the direction different types of polarization can be introduced. In cases when the field oscillates on a plane with no changes over time, it is called linear polarization, while in cases of fields having the same amplitude but out of phase by $90^\circ$ degrees it is considered to be circular as shown in fig. 2.2. In cases when the light consists of short wave packets with a mixture of polarizations the source is considered unpolarized [29].

The light field in free space can be described using eq. 2.5 written separately for field components in $x$ and $y$ directions. For propagation in the $z$ direction, the solution of the wave equation can be written as:

$$E(z,t) = E_{0x} \cos(\omega t - kz + \delta_x),$$  \hspace{1cm} (2.17)

$$E(z,t) = E_{0y} \cos(\omega t - kz + \delta_y),$$  \hspace{1cm} (2.18)

$$E(x,y,z,t) = E_x i + E_y j,$$  \hspace{1cm} (2.19)

where $E_{0x}$ and $E_{0y}$ are the maximum amplitudes, $\omega t - kz$ is the propagation component in $z$ direction and $\delta_x$ and $\delta_y$ are phases of $x$ and and $y$ components respectively. Equations above can be rewritten in terms of a polarization ellipse equation, which is usually used to describe the polarization state of the wave:

$$\frac{E_x^2}{E_{0x}^2} + \frac{E_y^2}{E_{0y}^2} - 2 \frac{E_x E_y}{E_{0x} E_{0y}} \cos \delta = \sin^2 \delta,$$ \hspace{1cm} (2.20)

$$\delta = \delta_x - \delta_y.$$ \hspace{1cm} (2.21)
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The cross term $E_x E_y$ is associated with the rotated ellipse and elliptical parameters in eq. \ref{eq:2.20} are connected to major and minor axes of polarization ellipse, angle of rotation and the ellipticity angle [29].

2.2 Light scattering

Light scattering is a term referring to the interaction of light and matter. When light is incident on any ensemble of particles (crystals, aerosols, molecules, atoms etc.) it is “deflected” in directions deviating from an incident angle. While propagating through material atoms and molecules behave as oscillators or electric dipoles. When light interacts with them, dipoles absorb and re-emit light at the same frequency, resulting in elastic scattering. In cases when light frequency matches the resonant frequency of the material, re-emitted light is of a different frequency, known as inelastic scattering. One of the examples of inelastic scattering is Raman scattering, when light is scattered by optical phonons (vibrational and rotational states of polarizable molecules) and yields scattered photons of energy diminished by transition energies. Frequencies of these photons are located around the incident frequency and called Stokes and anti-Stokes lines [29].

Elastic scattering in low-scale structures is dependent on light frequency and particle size. For particles much smaller than the wavelength of the incident light, Rayleigh scattering occurs. In that case the intensity of scattered light is inversely proportional to the fourth power of the light wavelength ($\sim \lambda^{-4}$) [1, 29]. Initially, Rayleigh scattering was attributed to molecular behavior, but it was shown by A. Einstein and M. Smoluchowski that it can also be applied to microscopic volumes of matter (volumes smaller than $\lambda^3$) with refractive index varied due to density, temperature and pressure fluctuations. The intensity $I$ can be written as:

$$I = I_0 \cdot \frac{1 + \cos \theta^2}{2R^2} \cdot \left(\frac{2\pi}{\lambda}\right)^4 \cdot \left(\frac{n^2 - 1}{n^2 + 2}\right)^2 \cdot \left(\frac{d}{2}\right)^6,$$

where $I$ is intensity of scattered light, $I_0$ is incident light intensity, $\theta$ is scattering angle in degrees, $R$ is distance to the particle, $\lambda$ is wavelength of the light, $n$ is refractive index and $d$ is a particle diameter [30].

Cases, when the scatterer size is comparable to or larger than the light wavelength ($\sim \lambda^3$), can be described by Mie’s theory of scattering. The Mie solution of Maxwell equations describes the light scattering on a spherical particle. In Mie’s theory, scattered electric and magnetic fields are represented as infinite series in the vector spherical harmonics with weight coefficients. The spherical harmonics include the angle-dependent functions expressed with Legendre polynomial series [29]. As the size of the scatterer further increases, Mie’s theory converges to geometric optics and light is considered a ray.
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Re-emitted light waves in materials are called secondary waves and depending on the medium state and condition they can be in phase (ordered crystal media) or non-phase correlated (disordered media). In cases when light is transmitted through material constructive interference occurs.

Elastic scattering in bulk materials can be calculated using simpler ray or geometric optics, for example reflection, refraction, transmission etc. When light is transmitted through the boundary of two bulk materials with different refractive indexes $n_1$ and $n_2$, the direction of the resulting light is differing from incident light, due to refraction. Additionally, part of the input light is reflected from the interface. The relation angle of refraction to the angle of incidence can be described with Snell’s law [29]:

\[
\sin(\theta_i)n_1 = \sin(\theta_t)n_2, \tag{2.23}
\]

\[
\theta_i = \theta_r = \theta, \tag{2.24}
\]

where $n_1$ is the refractive index of material that light is incoming from, $n_2$ is the refractive index of material light gets transmitted through, $\theta_i$ is the angle of incidence, $\theta_t$ is the angle of refraction and $\theta_r$ is the angle of reflection [29]. As seen from eq. 2.25 light is reflected at the same angle as incident light and can be written as $\theta$. The index of refraction can be described as the coefficient of change of speed of light in relation to the speed of light in a vacuum:

\[
n = \frac{c}{v}, \tag{2.25}
\]

where $c$ is the speed of light in vacuum and $v$ is the speed of light in the medium. If the incident medium has a larger index of refraction, then the angle of transmitted light is increased. Usually, the larger index medium is called internal, since air ($n = 1$) is usually the surrounding or external medium. From eq. 2.23 it can be seen that when the incident angle reaches a critical point the angle of refraction is equal to $90^\circ$. It is called total internal reflection, which means that in that case all light is reflected, which creates a basis for wave guiding effect [29]. Waveguides are structures specifically engineered to transport electromagnetic waves with minimal loss of energy by total internal reflection. In optics waveguides usually consist of dielectric material with a high index of refraction surrounded by a material with a lower index of refraction, guiding light via total internal reflection. It is important to note that Snell’s law is applied for smooth surfaces, which means that in cases of rough surfaces, it is applied locally and needs to be calculated for each localized area.

Another way to describe light refraction is the phenomenon of diffraction. According to the Huygens-Fresnel principle every point on a wavefront is a source of secondary waves that can interfere upon propagation. Diffraction phenomena can describe light bending behind the object’s edge or blurred shadows.
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Figure 2.3: Light distribution for: a) ordered structure, b) Transparent wood (assemble of quasi-ordered structures). The top right corners show the side profile of distributions.

via scattering on an object, followed by interference, which differs from shadow expected by geometrical optics [29].

There are multiple types of diffraction, which depend on the system where it occurs: aperture, single slit, multiple slits and diffraction gratings (dispersive structure made of periodic elements). When a plane wave is transmitted through the diffractive grating, following the Hyugens-Fresnel principle, every point of the wavefront is a point source for secondary waves that can interfere constructively or destructively, creating interference maxima, also known as diffraction orders. They can be described by the following:

\[ d(\sin \theta_i - \sin \theta_m) = m\lambda n, \]  

(2.26)

where \( d \) is the spacing between slits, \( \lambda \) is wavelength of incident light, \( m \) is an integer number, \( n \) is the refractive index at wavelength of incident light, \( \theta_i \) and \( \theta_m \) are incident and diffraction order angles respectively [29].

In the case of diffraction on periodic gratings, one can see the image shown in fig. 2.3, the spots of constructive and destructive interference with sharp edges. However, in the case of quasi-ordered gratings with different spacing and layered on top of each other the output image does not have sharp orders but it conserves the overall shape of the profile. Figure 2.3b shows the light distribution after the transparent wood sample that behaves as an assembly of quasi-ordered diffraction gratings.

2.3 Light losses

Light absorption is the process in which optical energy is converted into another form of energy. The absorption can be divided into two categories:
intrinsic and extrinsic. Intrinsic absorption is a basic property of the material, while extrinsic absorption results from impurities and structural defects in a material. In the case of semi-transparent medium absorption can be quantified with an absorption coefficient. The absorption coefficient describes the fraction of the power lost per unit length. It depends on the wavelength and is often represented with absorption spectrum [29].

The power loss can be quantified using modified Beer-Lambert law which can be in two following ways:

\[ T = \mu_a d = \log_{10} \frac{I}{I_0}, \]  

(2.27)

\[ I = I_0 e^{-\mu_a d}, \]  

(2.28)

where \( I_0 \) is the intensity of the incident light, \( I \) is the intensity of transmitted light, \( T \) is transmittance, \( \mu_a \) is attenuation coefficient and \( d \) is the sample thickness. This form of Beer-Lambert law is applied for scattering materials and is based on a multipole diffusion approximation [29].

Another source of light losses in a material is haze. Whenever light propagates through the material it is affected by irregularities within it, such as structure defects, particles dispersed, or air volumes in media. Small particles scatter light at a wide angle, and the amount of light scattered this way is called haze. Haze can be measured using the integration sphere by measuring references with a white standard or light trap and the same measurements with the sample in place. Based on these measurements haze can be quantified using the following equation:

\[ H = \frac{T_3}{T_2} - \frac{T_4}{T_1} \times 100\%, \]  

(2.29)

where \( T_1 \) and \( T_4 \) are reference measurements with white standard and light trap correspondingly, \( T_2 \) and \( T_3 \) are measurements with the sample in place and white standard or light trap. It is important to note that for highly scattering materials one needs to choose samples of the right thickness and incident beam of the right size in order to avoid loss of ballistic photons and to let all light in the integration sphere.

2.4 Light amplification

Light amplification is the process of increasing the intensity of an electromagnetic wave. There are three main types of light amplifications: parametric, scattering and laser amplification. Parametric and scattering light amplification is related to the effects of non-linear polarization. Laser amplification is based
on the stimulated emission of radiation and can be described with the following equation:

\[ I = I_0 e^{\gamma d}, \]  \hspace{1cm} (2.30)

where \( I \) is the intensity of transmitted light, \( I_0 \) is the intensity of the incident light and \( \gamma \) is the gain coefficient, depending on which different cases can be described. When the gain coefficient value is equal to zero material is considered fully transparent with no losses occurring, in cases when the value is below or above zero, absorption or amplification occurs correspondingly. As can be seen from eq. 2.30 take the same form as the exponential form of Beer-Lambert law.

Stimulated emission is the process in which the incoming photons of a specific wavelength interact with an electron in an excited state dropping it to ground level or lower energy level. That process releases energy in a form of a photon with wavelength, direction and polarization of the incoming photon. The case when pumping energy excites more than half of the atoms from the ground to an excited state is called population inversion. Then the active media releases the energy of excited states via electromagnetic radiation, which leads to the amplification of optical power. When the output is dominated by photons released via stimulated emission the lasing threshold is reached, creating laser [29].
Chapter 3

Transparent wood: basics and functionality

This chapter gives an overview of transparent wood, the focus material of this work. TW is a highly scattering structure that conserves hierarchical and anisotropic structures from native wood. In this chapter, we go over the fabrication process and structure features of TW, as well as how light propagation in it can be modeled and how TW can be used as a host for functional additives.

3.1 Transparent wood

Transparent wood is a natural wood that went through a chemical modification that made it transparent to visible light by lignin removal. Natural wood consists of different chemical compounds mainly cellulose, lignin and hemicellulose. Most of the volume is consisting of cellulose, which takes up to 40 – 50% of the weight content depending on wood species. In wood, cellulose takes the form of fibrils. The cellulose fibrils are connected to each other and lignin by hemicellulose, a polysaccharide compound, which also keeps cellulose fibrils from aggregating in bigger structures. Wood weight content consists of 20 – 40% of hemicellulose. Lignin is an aromatic compound located in cell walls and corners, and it provides mechanical stiffness to the whole wood structure [20, 40–45]. Cellulose and hemicellulose are optically transparent in the visible range, and most of the absorption (90 – 95%) in the visible range is attributed to lignin (hence the yellow-brownish color of native wood), and the rest of absorption is coming from chlorophyll, tannins and other compounds. By removing lignin (delignification process), or by deactivating chromophores in lignin (bleaching process), most of the absorption can be removed. The delignification process does not remove all lignin, leaving around 3 – 5% of lignin, due to imperfection of the process and due to wood losing stiffness if all lignin
CHAPTER 3. TRANSPARENT WOOD: BASICS AND FUNCTIONALITY

Figure 3.1: a) SEM image of balsa wood structure, b) SEM image of balsa wood cross-section, c) 3D model of wood structure

Depending on the method and the process times of transparent wood preparation, different types of TW can be produced. The resulting samples mainly differ in transparency and haze. Low haze TW has a strong interfacial adhesion between the wood structure and polymer matrix, which improves transmittance and lower scattering. Mid and High Haze TW, on the other hand, through the process of delignification have lower interfacial adhesion, which leads to the formation of interfacial gaps from shrinkage of the polymer matrix. The formed gaps increase the scattering in the TW structure, thus increasing haze and lowering transmittance. This property affects the further use of TW for functionalization.

After native wood goes through either of two modification methods it loses its color and becomes white (due to air-filled voids inside that lead to very high scattering). The chemical treatment does not affect the structure of the wood, keeping the original morphology. The wood structure can be seen in fig. 3.1 consists of cellulose nanofibrils (5 – 7 nm in diameter), that form wood fibers (5 – 35 µm in diameter), vessels (150 – 250 µm in diameter), that are aligned parallel to each other, and wood rays (5 – 35 µm in diameter), which are aligned perpendicularly to fibers and vessels. To achieve transparency, a wood template
is filled with polymer with matching refractive index, for example polymethyl methacrylate (PMMA) or thiolene [10, 17, 18, 23].

The resulting transmission of TW can reach values up to 90%, depending on sample thickness, preparation method, or wood species used for preparation. Losses in TW are attributed to residual lignin and high scattering. After polymer infiltration, due to incompatibility, polymer shrinkage and depending on the thickness of the sample, air voids can be formed. Additionally, the refractive index of TW cannot be equated to the refractive index of cellulose (∼1.525–1.596 depending on propagation direction), since TW also consists of residual lignin (∼1.61), hemicellulose (∼1.532) and other chemical compounds. That creates certain challenges with choosing polymer with matching refractive index [25, 51].

To summarize, TW is an optically transparent, highly scattering material that conserves the original structure of native wood, which is prepared by chemical modification of lignin and filling with refractive index matching polymer.

### 3.2 Experimental techniques for TW characterization

To characterize materials and light behavior in them, researchers use different experimental techniques and tools, depending on what property needs to be investigated. In order to measure the transmission and absorption of a
TW sample, one can use the measurement routine established by the American Society for Testing and Materials ASTM D1003-13 for plastics and polymers [19]. This method uses an integrating sphere with multiple ports in use: the entrance for a light source, the entrance where the detector is installed, and the entrance where a white standard or light trap can be installed.

![Figure 3.3: (a, b) Transmittance spectra of the nonacetylated and acetylated TW in the visible range. (c, d) Fitting for nonacetylated and acetylated TW at 550 nm wavelength and visibility of symbol “W” through TW of different thickness.](image)

Transmittance was measured by placing the TW sample at the entrance port, with light at normal incidence to the surface. The ratio of intensity with and without the sample defines transmittance:

$$T = \frac{I_0}{I} \times 100\%.$$  \hspace{1cm} (3.1)

The measurement of transmittance was performed for nonacetylated and acetylated TW using the broadband light source, showing how wood modification can improve the optical properties of the transparent wood. Due to highly scattering structure of TW, the losses are described with attenuation coefficient instead.
of absorption. The attenuation coefficient has dependency on absorption and anisotropic diffusion coefficient, which is a combination of scattering and absorption in different directions within the material. As can be seen from fig. 3.3 there is an exponential relationship between total transmittance and sample thickness, and by implementing modified Beer-Lambert’s law the attenuation coefficients were calculated to be 1.75 and 0.71 at 500 nm for nonacetylated and acetylated TW samples respectively [Paper A].

![Figure 3.4: Setup for measurement of transmittance and haze in transparent wood: a) thin sample on top of input port with a beam size smaller than the input port diameter; b) thin sample placed on top of input port with a beam size larger than or comparable to the input port diameter; c) thick sample placed on top of input port with a beam size smaller than the input port diameter; and d) sample with thickness larger than the transport mean free path (TMFP) so that no ballistic photons are observed.][18]

Haze (optical scattering), is measured using an integrating sphere, and this haze tells how much information is lost after the sample. To measure haze, four measurements are performed as can be seen in fig. 3.4 the intensity measurement with no sample and output with a white standard in place \( T_1 \), measurement of the sample and white standard \( T_2 \), measurement of sample and light trap (to measure scattering without including ballistic photons, \( T_3 \)), and measurement only with light trap \( T_4 \). Then haze can be calculated by taking the ratio of scattered intensity without the inclusion of ballistic photons to total intensity:

\[
H = \frac{T_3}{T_2} - \frac{T_4}{T_1} \times 100%.
\] (3.2)

Due to the anisotropic structure of TW, the scattering from the sample depends on the fiber direction [46, 52, 53]. That anisotropy can be observed by measuring light distribution after the sample for different TW sample orientations. The measurement is performed using the setup in fig. 3.6 the circularly polarized laser source (obtained using a quarter wave plate), incident at the sample fixed in the middle of the rotating base with a power meter. That
Figure 3.5: Transmittance (blue) and haze (orange) of transparent wood. The 500-600 nm range was measured with broadband white light. The 400-500 nm range was measured in 10 nm steps with grating selected narrow linewidth light allows to measure of light distribution after the sample for two main fiber alignments. It was shown, that angular distribution for samples aligned in vertical distribution is visibly broader than horizontal alignment \[12\].

The measurement of the refractive index of the TW sample can be performed following the ASTM D1003. The sample of TW was immersed in liquids with different refractive indices and shined on by an unpolarized light source, and intensity at the output was integrated over the collected spectrum \[25\]. That allows researchers to estimate the refractive index of wood, but to get the exact RI value methods that destroy the sample are required (since the TW without polymer is highly porous).

To further study on the anisotropic structure of transparent wood the effect of the polarization state of incident light on light distribution was investigated. The measurement was performed by shining an unpolarized broadband LED with diffusing glass plate (to avoid interference) through an 8 mm TW sample with light distribution collected by a CCD camera as seen in fig. 3.7 a). Then the Stokes parameters at each point of the sample were used to estimate the state of polarization with the spatial resolution of 5\(\mu\)m. Additionally, measurements using linearly polarized light (633 nm He-Ne laser) and com-
Figure 3.6: Schematic diagram of experimental setup for measurement of light distribution

Commercial polarimeter PAX1000VIS from Thorlabs were performed, which showed agreement for both methods.

The intensity maps collected via CCD camera using different positions of quarter-wave plate and linear polarizer, which was then aligned using the dark reference mark seen in fig. 3.7 a). Using modified nearest neighbor pixel to use collect intensity values and calculate Stokes parameters of every pixel after the TW sample with following equations:

\begin{align}
S_0 &= I(0^\circ, 0^\circ) + I(90^\circ, 0^\circ), \\
S_1 &= I(0^\circ, 0^\circ) - I(90^\circ, 0^\circ), \\
S_2 &= 2I(45^\circ, 0^\circ) - I(0^\circ, 0^\circ) - I(90^\circ, 0^\circ), \\
S_3 &= 2I(45^\circ, 90^\circ) - I(0^\circ, 0^\circ) - I(90^\circ, 0^\circ),
\end{align}

where $S_n$ is a stokes parameter, $I(k^\circ, l^\circ)$ is intensity with a corresponding position of quarter-wave plate and linear polarizer. Calculated Stokes parameters can be used to describe polarization state of the light after the sample \cite{29}.

The distribution of state of polarization over CCD area, defined by the angle of rotation and the ellipticity angle of polarization ellipse, is uniform over the surface in terms of magnitude fluctuation. The wood vessels can be detected on the spatial distribution of degree of polarization (DOP) as the areas of the lowest values indicating low scattering regions as seen in fig. 3.7 a).
CHAPTER 3. TRANSPARENT WOOD: BASICS AND FUNCTIONALITY

Figure 3.7: a) A spatial distribution image was taken with CCD for the degree of polarization. b) Dependence of DOP on the orientation of fibers (and vessels) in the rotated TW balsa sample. The orientation angle is established relative to the horizontal axis of the lab frame, thus orientation angle of 0° - corresponds to the horizontal orientation of the vessels, and 90° - to the vertical. c) Dependence of DOP from the input linear polarization for different wood types measured with the commercial polarimeter.

The results obtained by averaging data over the surface of the CCD camera have shown that unpolarized light gains some degree of polarization as it propagates through the TW sample, achieving values around 50% DOP. Unpolarized light, which is a mixture of two orthogonal polarizations, becomes partially polarized due to anisotropic scattering, with strong scattering along the fibers, while perpendicular polarization is mostly unaffected [Paper B].

In the case of linearly polarized light, as shown in fig. 3.7 c) the DOP is decreased depending on the angle between the angle of light polarization to fiber orientation in the sample. Additionally, two local minima in DOP were detected, at angles 25° and 155° degree, where the DOP shows a significant decrease to 3% at the incident light polarization of 25° for balsa TW, while for the input polarization of 70° DOP is mostly 90-100%.

The source of that effect is the structural features of the material. TW
CHAPTER 3. TRANSPARENT WOOD: BASICS AND FUNCTIONALITY

Figure 3.8: Schematic representation of the cell wall of a tubular wood fiber (lumen pore space in the centre) with three layer of microfibrils (S1 - S3). E – vector of electric field, P – local dipole

consists of mostly cellulose (80%), located in microfibrils (around 4nm in diameter) in fiber walls (fig. 3.8). There are three layers of fibrils S1, S2, and S3, oriented at different angles around the larger fiber as they twist helically around the cell [54]. Fibrils in the thickest layer S2 are always oriented in the right handed helix along the fiber longitudinal direction, while microfibrils in S1 and S3 layers can be oriented in opposite helical directions [54]. Cellulose crystallites present in the fibrils consist of highly oriented cellulose molecules with long-range order [55]. Cellulose has permanent electric dipole moment due to assymetric nature of the polar glucopyranosyl monomers, the chemical polarity of the cellulose chainsm and the parallel, non-centrosymmetric structure of the chains in native cellulose inside cellulose crystals [56]. These dipoles can efeciently scatter the light of polarization oriented along the dipole axis. The dipoles located on layers S1 - S3 scatter the light most efficiently at angular directions coinciding with the linear polarization direction of the incident light. Thus, the DOP dependence on incident polarization seen in fig 3.7c) is caused by light scattering by microfibrils in the secondary layers. Since depending on the wood species the value of microfibril angles can vary, the DOP of the light varies for different wood species [57] [Paper B].

3.3 Modelling of transparent wood

Based on experimental results the computational model of TW and light behavior can be introduced. The results of modeling can be compared with the results of performed experiments to characterize TW or to design material
tailored for specific requirements. Additionally, modeling allows us to avoid destructive methods and bypass the sample preparation process.

Figure 3.9: a) Schematic diagram of sizes and directions of TW COMSOL modeling with SEM images. Three samples of different TW thicknesses, 1, 2, and 3 mm, are shown by light blue, blue, and dark blue, respectively. b–d) The modeling process from SEM image to TW models.

The light propagation can be simulated using different computational methods. The most straightforward approach that we implemented, is the finite element method (FEM). FEM is a generic method based on subdividing a large system into smaller parts (finite elements) by discretization it into the mesh. Then the solution is found for each element instead of solving the whole system in one go. This method's advantage is that it is a strict solution based on analytical solution and thus is very precise. However, for complex systems the mesh has to be finer, increasing the computation time and memory requirements. Another approach is statistical, for example, Monte-Carlo (MC) method, which is a computational algorithm based on repeated random sampling computed to find statistically most likely outcome. That method can be used for any problem that has a probabilistic interpretation or distribution, for example, light scattering in the material. In order to simulate light scattering in media using the MC method, the probability distributions of scattering processes are required [58–61].

In this work, FEM method was implemented in COMSOL Multiphysics 5.5 software. The mesh was based on SEM images of processed wood structure.
Due to strong scattering in wood structure, the light propagation is taking the shape of the cone, as seen on fig. 3.12 so the geometry of FEM model was generated in trapezoid shape to decrease memory requirements. The 2D model was generated for samples of 1, 2 and 3 mm thick samples, at an angle of 45° to the ray alignment, in order to compare results with experiment measuring light distribution, which was performed with the same parameters. The mesh was generated by analyzing SEM image using the Trainable Weka Segmentation plugin for ImageJ software [62]. Figure 3.9 illustrates the schematics of the modelling process. Each cell is represented as closed curve consisting of polygons with a limited number of connecting points. Due to complexity of
wood structure and elements that can be on several micron scales, the mesh coordinates data required a lot of memory to generate the model. In order to resolve that challenge TW model with larger distance between each polygon was used to reduce the memory requirement. The TW models with cortex distances of 5, 7, 9 and 12 µm were generated and compared to high precision model. Based on analysis of results the 7 µm vortex distance was chosen for the simulation.

Figure 3.12: Ray tracing for different TW thicknesses: a) 1 mm, b) 2 mm, and c) 3 mm. The optical power transported by optical rays ranging from 0 to $5 \times 10^{-5} \text{Wm}^{-1}$ is represented by color bar encoding from black to red. In these simulations, the thiol-ene polymer matrix has RI = 1.56, and the cellulosic wood substrate has RI = 1.54

COMSOL Multiphysics have two ways to simulate light propagation: wave optics module that uses rigorous solution of Maxwell equations and solves simulation in frequency domain, which should be used for general case, but requires large amount of memory; and ray tracing module, which is more applicable for simulation of system of larger sizes, at the millimeter scale. Ray tracing module ignores scattering on small-scale (Rayleigh scattering), leaving only larger scale scattering (Mie scattering) to analyze the output distribution. Since in TW, the large-scale scattering is dominant, and as shown on fig. 3.10 ray tracing and wave optics modules converge to same solution. In order to be comparable with experimental results the half-circle with 15 cm radius was generated to emulate collection of light distribution at the same distance as experiment. The resulting light distribution (fig. 3.12) and ray tracing shows that light distribution is skewed in direction of wood ray alignment, attributed to its wave guiding effect [18, 63]. By setting the refractive index of polymer to match the refractive index in experiment ($n = 1.56$), the effective refractive index of wood scaffolding was estimated to be $n = 1.54 \pm 0.005$ for 633 nm wavelength as seen on fig. 3.11. It is important to note that the estimated refractive index is not the refractive index of cellulose, but effective refractive index of the TW sample (cellulose, hemicellulose, residual lignin etc.) [Paper C].


3.4 TW functionalization

The structure of wood, as mentioned earlier, mainly consists of tube-like fibers, ray cells and vessels, with wood ray cells oriented perpendicular to aligned fibers and vessels. That allows infiltration of active materials in order to functionalize TW samples [23, 24].

One of the examples of transparent wood functionalization is infiltration with active dye [27]. In TW biocomposites, dye is mostly distributed on cell walls, rather than in voids, which is visible on confocal fluorescence micrographs (fig. 3.13c)). The dye is homogeneously distributed in cells walls throughout the wood structure, with negligible amount in the polymer filled voids. In this work, we investigate the TW qualities as a host of rhodamine 6G laser dye and its possible application. The functionalized TW samples were prepared by delignifying native balsa wood, which increases its porosity, surface area, and hygroscopicity when compared to native wood, increasing the adsorption capacity [64–66]. Then it was submerged in acetone solutions of Rh6G ranging in concentration from 25 to 200 µM. The next step was to wash the resulting sample with acetone to remove excess dye and the infiltrated with PMMA [67]. Rh6G infiltrated TW samples had concentrations ranging from 5.4 to 36.8 mM, which is significantly higher than reported values in other solid hosts as seen on Table 1 [67–69].

The host quality of TW for hosting dye at high concentrations was analysed using the quantum yield (QY) measurement. The measurement was performed using the integration sphere and 500 nm light source to collect the spectra of undoped TW reference and dye-doped TW sample. By calculating ratio of emission to absorption QY can be quantified:

$$QY = \frac{q_{\text{emission}}}{q_{\text{absorption}}} \tag{3.7}$$

where $q_{\text{emission}}$ is number of emitted photons and $q_{\text{absorption}}$ is number of absorbed photons. In case of spectral measurement these values can be obtained by calculating area of the spectra. The decrease in QY value corresponds to aggregation-induced quenching, formation of statistical traps, or losses from inner effects [70, 71]. The experiment QY measurements for low concentration samples can be adjusted for inner effects, but currently there are no established methods for high concentration samples, which is the case in this work [72, 73].

As seen from fig. 3.13 QY of Rh6G infiltrated TW samples is decreasing (72 to 44 %) with increase in dye concentration. However, that decrease is not related to aggregation of dye, because aggregation affects the electronic energy levels, which can be seen on absorption spectra. Absorption spectra presented on fig. 3.14 does not show changes in spectra that can be attributed to aggregation, like shoulder peak around 500 – 510 nm [67, 69]. From that it can be concluded
that there is no strong aggregation. The decrease in QY is explained by formation of statistical traps, where weakly interacting monomeric dyes generate non-radiative relaxation pathways \[71, 72\]. That can not be confirmed by observing absorption spectra, but statistical traps affect the fluorescence lifetime. The fluorescence decay curves are presented on fig. 3.14c) and fluorescence lifetimes can be seen in d). The adsorbed dye in wood structure interacts with different chemical environments, which affects the decay lifetime resulting in a range of decay rates. Instead, we take the average decay lifetime estimated from the slope of the following equation \[74\]:

\[
I(t) = I_0 e^{(-t/\tau)}, \tag{3.8}
\]

where \(I\) is measured intensity, \(I_0\) is the intensity at \(t = 0\), \(t\) is the time in ns,
Figure 3.14: a) Experimental fluorescence quantum yield of Rh6G-TW samples versus dye concentration in wood. b) Normalized absorption spectra of Rh6G-TW samples. c) Characteristic fluorescence decay curves of Rh6G-TW. Inset shows magnification of the marked area. d) Fluorescence lifetimes of Rh6G-TW (average of six measurements)
CHAPTER 3. TRANSPARENT WOOD: BASICS AND FUNCTIONALITY

Table 1. Dye concentration, dye per host mass, expected quantum yield and lifetime decay of different solid dye hosts

<table>
<thead>
<tr>
<th>Host</th>
<th>( C_{\text{host}} ) [nm]</th>
<th>( \text{Rh6G per host mass} ) [( \mu \text{mol. g}^{-2} )]</th>
<th>Exp. QY [%]</th>
<th>( r ) [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delignified Wood (in Rh6G)</td>
<td>5.4 ± 0.2</td>
<td>3.4 ± 0.1</td>
<td>72.0</td>
<td>5.86 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>12.0 ± 1.0</td>
<td>7.0 ± 0.7</td>
<td>69.0</td>
<td>6.25 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>14.4 ± 0.8</td>
<td>9.1 ± 0.5</td>
<td>60.7</td>
<td>6.06 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>18.6 ± 1.5</td>
<td>11.8 ± 1.0</td>
<td>56.7</td>
<td>5.89 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>19.0 ± 1.0</td>
<td>11.0 ± 0.8</td>
<td>51.5</td>
<td>6.00 ± 0.39</td>
</tr>
<tr>
<td></td>
<td>26.8 ± 1.2</td>
<td>10.0 ± 0.7</td>
<td>49.0</td>
<td>5.88 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>29.7 ± 1.1</td>
<td>18.8 ± 0.7</td>
<td>44.3</td>
<td>5.48 ± 0.27</td>
</tr>
<tr>
<td></td>
<td>39.8 ± 1.7</td>
<td>23.2 ± 1.1</td>
<td>44.9</td>
<td>5.30 ± 0.16</td>
</tr>
</tbody>
</table>

| Microcrystalline Cellulose | -                           | 1.00                                                         | 79*          | 3.2          |
|                            | -                           | 2.00                                                         | 68*          | 3.0          |
|                            | -                           | 4.00                                                         | 53*          | 2.8          |

| Silk Fibroin*              | ~16.0                       | -                                                            | 10           | 1.2          |
|                            | ~28.8                       | -                                                            | 5            | 6.8          |

| Type II Rh6G-silica*       | 0.14                        | -                                                            | 71           | 5.53         |
|                            | 0.5                         | -                                                            | 52           | 5.46         |
|                            | 1.1                         | -                                                            | 22           | 5.26         |
|                            | 1.6                         | -                                                            | 21           | 4.17         |

* Fluorescence quantum yield adjusted for inner filter effects.

and \( r \) is the fluorescence lifetime.

Figure 3.15: Emission spectra of dye-doped TW under increasing pumping intensity. The inset shows a magnified view of the emission spectra of Low Haze TW
The average lifetime decreases from 6.25 ns for 12.6 mM samples, to 5.35 ns for 36.8 mM samples. That results correspond with formation of statistical traps due to decrease in distance between molecules [74]. That indicates that distribution of dye is not random, as formation of statistical traps only occurs with increase of concentration for the constant host volume.

Another effect responsible for decrease of QY is inner effect, most likely the reabsorption effect. That happens due to overlap of absorption and emission bands of Rh6G dye. Since increase in dye concentration increases optical path length inside TW due to increased scattering, increasing the chances of reabsorption occurring. Thus, the measured QY is decreasing with increase of reabsorption rates in higher concentration samples [72]. The reabsorption is also causing redshift of spectra due band overlap for shorter wavelengths [Paper D].

It is important to notice that when TW is used as a host of active dye, the resulting function of material needs to be taken into account. While Low Haze TW is more efficient for fluorescence without light amplification due to lower haze which leads to higher spectral brightness. However, for applications in which the light amplification takes place, e.g. lasing, Mid and High Haze TW, show better performance due to higher scattering as shown in fig. 3.15, increasing light path length increasing the probability of active dye absorbing the incident light [Paper F].

To conclude the TW is a very effective host, capable of holding lasing dye at higher concentrations than other solid hosts due to adsorption on cell walls. With increase of concentration Rh6G does not show signs of aggregation-induced quenching but is affected by formation of statistical traps and reabsorption.
Chapter 4

Lasing in transparent wood

4.1 Random lasers

The concept of random lasing was first proposed by Letokhov et al. in 1968 [34]. The feature of random lasing is that while the operation principle of random lasers is like a conventional laser, lasing occurs through the process of amplification and feedback. Regular lasers use an optical cavity that consists of a mirror and partial mirror to provide feedback, and gain medium provides light amplification. When gain becomes higher than losses lasing occurs. While the gain is generated in the same way, the feedback in random lasers is provided by scattering [37].

So far most of the presented random lasers were based on random, high-scattering media, such as powders or scatterers randomly distributed within active media. By scattering in media, the light can form a closed loop, generating a coherent emission, or the gain occurs without creation of a loop, generating incoherent emission [37, 75–80].

Random lasers have shown a wide use in bioimaging and tumor detection, for purposes of sensing nanostructural changes in bone structure and measurement of dopamine at very low concentrations, etc [81, 82]. Random lasers also can be used to map cancer tumors due to their difference in scattering [83].

Another property that can be observed in random lasers, but not in traditional lasers is low coherence. Wave sources are considered coherent when they have identical frequency and waveform. That property was initially shown in a double-slit experiment by Thomas Young. There are two types of coherence: spatial and temporal coherence. The correlation of two waves at a different point in space is described by spatial coherence and the correlation of two waves at different points in time is described by temporal coherence. [29]
CHAPTER 4. LASING IN TRANSPARENT WOOD

4.2 TW-based quasi-random laser

Due to the host properties and hierarchical structure of transparent wood, it acts as a perfect template for a random laser. In recent years, it was demonstrated that TW can be functionalized with the use of different additives. Transparent wood can be doped with different materials and can have several properties: TW with properties of IR shielding (doping with $Cs_xWO_3$), magnetic $Fe_3O_4$ nanoparticles, luminescent magnetic additives, quantum dots, lasing dyes, etc [23, 24, 84].

![Figure 4.1](image.png)

**Figure 4.1:** a) Schematic layout of pumping set-up for investigation of lasing properties of Rh6G-TW. b) Illustration of the wave-guiding effect of wood fibers in TW. c) Emission spectra of a 5.4 mM sample pumped with increasing pumping energies from a second harmonic generation Nd:YAG laser.

Doping TW with lasing dye shows that the resulting system can generate lasing due to scattering on wood scaffolding. However, the structure of wood is neither ordered or disordered, since while there is an overall structure and typical sizes of wood elements, they vary due to imperfection of natural ordering. That means that in concept, TW laser works the same way the random laser does (feedback provided by scattering), but differently due to the difference in structure and wave guiding effect of fibers, which aligns part of the emission [18, 63]. Because of that the resulting system is referred to as quasi-random laser [27].

The TW quasi-random laser setup is consisting of the following elements: Rh6G dye-doped TW sample is pumped by a 532 nm 1 Hz pulse SHG Nd:YAG laser shaped into a rectangular pumping line with the use of a beam expander and plano-convex cylindrical lens, as seen on Fig 4.1. One of the output sides is coupled into the Andor spectrometer using the lens system. The figures present the spectra of the laser at different pumping power range from 23 to 528 $\mu$J. It is important to mention, that the total energy of the TW laser was not measured due to it lasing in all directions, with preference in direction of fiber alignment.
Figure 4.2: a) Characteristic lasing spectra of Rh6G-TW samples. b) Full width at half maxima (FWHM) of selected Rh6G-TW samples as a function of pumping energy. c) Output energy vs pumping energy of Rh6G-TW samples. d) Comparison of output energy from Rh6G-TW samples with different dye concentrations pumped with 446 µJ (average of three samples, six positions).

Table 2. FWHM, centroid, lasing threshold and efficiency of samples with different dye concentrations

<table>
<thead>
<tr>
<th>Sample (dye conc)</th>
<th>FWHM [nm]</th>
<th>Centroid [nm]</th>
<th>Threshold [µJ]</th>
<th>Slope Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.4 mM</td>
<td>3.57 ± 0.54</td>
<td>568.6 ± 0.9</td>
<td>134.8</td>
<td>0.72</td>
</tr>
<tr>
<td>12.6 mM</td>
<td>3.22 ± 0.40</td>
<td>572.2 ± 0.9</td>
<td>153.3</td>
<td>0.15</td>
</tr>
<tr>
<td>14.4 mM</td>
<td>4.15 ± 0.71</td>
<td>573.8 ± 1.6</td>
<td>143.4</td>
<td>0.12</td>
</tr>
<tr>
<td>18.8 mM</td>
<td>3.99 ± 0.38</td>
<td>573.8 ± 1.6</td>
<td>156.6</td>
<td>0.12</td>
</tr>
<tr>
<td>19.8 mM</td>
<td>4.43 ± 0.39</td>
<td>575.8 ± 1.9</td>
<td>129.4</td>
<td>0.11</td>
</tr>
<tr>
<td>26.8 mM</td>
<td>4.34 ± 0.42</td>
<td>577.0 ± 2.0</td>
<td>129.6</td>
<td>0.14</td>
</tr>
<tr>
<td>29.7 mM</td>
<td>4.55 ± 0.53</td>
<td>576.5 ± 1.5</td>
<td>117.5</td>
<td>0.17</td>
</tr>
<tr>
<td>36.8 mM</td>
<td>5.26 ± 0.38</td>
<td>577.9 ± 1.7</td>
<td>104.4</td>
<td>0.21</td>
</tr>
</tbody>
</table>

There was previous research performed to investigate the origin of the optical feedback in quasi-random laser, concluding that every fiber act as an
independent resonator, providing multimode lasing of Rh6G-TW sample [38]. Additionally, the coherence of the quasi-random TW laser was investigated, showing low coherence, which is applicable in areas where high brightness and low spatial coherence are required, for example, speckle-free imaging [38].

Figure 4.3: Spectral measurement of TW pseudo-random laser with deposited silver mirror pumped by SHG Nd:YAG laser at different pumping power

In this work, the lasing properties of quasi-random TW laser with different Rh6G concentrations were investigated, using TWs ability to host high concentrations of dye without aggregation. As can be seen from figure 4.1c), at lower pumping energies the TW laser generates enhanced fluorescence with a wide emission peak, but with an increase of pump energy, the narrow linewidth emission is generated. With the increase in dye concentration, the laser emission broadening and redshift were observed. However, the broadening of emission (from 3.57 to 5.26 nm FWHM) is still below 6 nm, distinctive for lasing dyes in low-quality cavities. It was expected that FWHM would decrease, which can be explained by the increase of resolved modes, which is confirmed by further experiments in which the mirror was attached to the back facet of the laser to increase the number of possible closed loops for laser generation. In case of an increase in pumping energy, the light penetration depth increases, leading to more fibers being illuminated increasing emission intensity, and a number of modes resolved.

The redshift of the emission spectra, observed in the fig. 4.2a), is characterized by centroid (center of gravity of the integral of the emission spectrum), which shifted from 568.6 to 577.9 nm, as can be seen on Table 2. It indicates the increase in dye-dye interactions due to the formation of energy traps,
caused by a decrease in the distance of dye distribution \[74\]. Improvements in laser performance, represented by the lower lasing threshold, output energy for different concentrations and different pumping powers are presented in fig. 4.1 and 4.2. From these, it can be concluded, that laser performance is improving with the increase in dye concentration, and even when the formation of statistical traps starts (18.6 mM), the enhancement of lasing continues to grow faster than the reduction from the formation of statistical traps.

Figure 4.4: Spectral measurement of TW pseudo-random laser with different R6G concentration with mirror attached to the back facet

Further research was made to validate the hypothesis that a quasi-random TW laser is an assembly of multiple microcavities acting as a single system. It was achieved by the introduction of the external resonator in a form of an attached mirror, which in addition to validation can show that the TW laser can be amplified. Two approaches were investigated - mirror deposition on the surface of the back facet of the Rh6G-TW sample, and placement of the mirror at the back facet.

The first method has shown that preparation of the TW surface for deposition is very challenging, due to the difference in rigidity of wood scaffolding and infiltrated polymer, reducing the quality of the surface with cellulose fibers being more resistant than polymer. Due to the roughness of the surface, the deposited mirror had a diffusive reflection, lowering the intensity of the light guided by fibers and leading to higher losses than in the case without the mirror. The spectra of the TW laser with deposited mirror can be seen in fig. 4.3.

In the second approach, the mirror was placed at the polished back facet, resulting in specular reflection, which can act as an external resonator, virtually increasing the size of the resonator, which increases the number of resolved modes due to the formation of a higher number of closed scattering loops within active media. At lower concentrations, visible peaks corresponding to new modes were detected, but the higher intensity and slight redshift imply that new modes, very close to the ones resolved without a mirror, appeared.
As concentration increases the new resolved modes can be detected (fig. 4.4), showing visible broadening and extra peaks on the spectra, as well as an increase in intensity.

![Figure 4.5: Spectral measurement averaged for 3 measurements with and without a mirror for a) 175 uM and b) 200 uM. Additional peaks indicate the generation of additional lasing modes. Average distance between modes resolved only for samples with mirror is lower by factor 1.5 – 2](image)

Detected peaks correspond to longer cavities, which can be described by an equation that shows the dependence of distance between modes on the cavity length \[29\]:

$$\Delta \nu = \frac{c}{2nL}$$  \hspace{1cm} (4.1)

where \(\Delta \nu\) is the distance between modes in frequency, \(c\) is the speed of light, \(n\) is index of refraction and \(L\) is the cavity length. From equation 4.1, it can be seen that cavity length is inversely proportional to the distance between modes. Figure 4.5 show detected peaks for samples with and without a mirror and in most cases, additional modes correspond to the appearance of longer cavities. Also, there are peaks corresponding to cavities of the same lengths, which were not achieving enough gain for lasing.

The linewidth of all samples is increasing with pumping power due to new modes being resolved. However, the FWHMs of all samples are below 6 nm, indicating lasing. Based on that results it can be confirmed that TW-based laser is acting as an assembly of microcavity lasers \[38\], which can be amplified by using a mirror that virtually expands cavity length \[Paper E\].

To summarize, TW can be functionalized with laser dye (Rh6G), creating a quasi-random laser, where optical feedback is provided by scattering on the cell walls of wood fibers, forming a closed loop. It shows high intensity, due to the
excellent host properties of TW, which allows doping with a higher concentra-
tion of dyes without aggregation. The laser can be further enhanced by adding
an external resonator in a form of a mirror that extends the active volume and
induces the formation of more closed-loop cavities, increasing intensity and re-
solving more lasing modes and confirming the hypothesis that TW-based laser
is an assemble of microcavity lasers.
Chapter 5

Conclusion

The dependence of light transmission in TW was investigated by performing the measurement using the integrating sphere on samples of different thicknesses. By implementing the Beer-Lambert’s law for light propagation, the attenuation coefficient for acetylated and nonacetylated TW was calculated, showing the possibility to tailor the optical properties of TW via the preparation process. The results of calculations were confirmed by comparison with measurements, showing that it can be used to estimate the attenuation in other anisotropically scattering materials.

Further investigation of TW has shown that the birefringence of the material is coming from the hierarchical structure of transparent wood, where microfibrils are affecting the passing light, changing its degree and state of polarization, which was measured over the area of TW samples and calculated using the developed model. To deepen the understanding of light behavior and to estimate the refractive index of wood scaffolding \((n = 1.54)\), the computational finite element method model was developed using COMSOL software and SEM images of wood structure. The model results were confirmed by comparison with experimental results and have shown the existence of a wave-guiding effect in TW structure, which can partially align light propagation. That model can be used for nondestructive estimation of the refractive index of different materials and calculation of light propagation in highly scattering media.

Transparent wood has shown excellent host properties, capable of holding high concentrations of Rh6G without aggregation when compared to other materials. That property allows TW to be functionalized with active dye, creating a highly scattering active media capable of achieving fluorescence and lasing.

Laser based on TW is working on principles differing from conventional lasers, achieving gain through scattering, characteristic encountered in random lasers, instead of reflections. However, due to the quasi-random structure of TW and its wave-guiding properties, the TW laser is considered to be a quasi-random laser, behaving as an ensemble of lasing microcavities.
CHAPTER 5. CONCLUSION

Additionally, it was shown that the TW laser can be further amplified by the introduction of the external cavity in a form of a mirror attached to the back facet, virtually expanding the active area and leading to a higher number of interactions and increasing the directionality of the TW laser. An increase in intensity and additional peaks indicate that the external cavity causes the resolution of a higher number of lasing modes, related to the same length and longer microcavities, confirming previous findings that the TW laser is behaving as an ensemble of lasing microcavities.
Chapter 6

Future work

The research of this dissertation can be followed by an investigation of the following topics:

- General analytical model of light propagation in TW.
- 3-dimensional computational model of transparent wood, most probably based on a statistical approach, such as the Monte Carlo method, based on the 2D model presented in this work.
- Improved surface preparation method that allows deposition of mirror capable of achieving same results as mirror placement.
- Further research on the introduction of the external resonator to TW laser and measurement of its total power.
- Investigation of polarization TW quasi-random laser emission and its dependence on input polarization.
Bibliography


42. Wiedenhoeft, A. C. & Miller, R. B. *Structure and function of wood* (CRC Press, 205).


