



Budapest University of Technology and Economics
Department of Physical Chemistry and Materials Science

BALÁZS BORBÁS

*UPCONVERTING NANOPARTICLES: ANTI-STOKES
PHOTON EMISSION AND ENERGY TRANSFER
PROPERTIES OF COMPOSITE THIN FILMS*

Supervisors: Zoltán Hórvölgyi, PhD
Borbála Tegze, PhD

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1 Introduction

The research presented in this paper was carried out at Budapest University of Technology and Economics, Department of Physical Chemistry and Materials Science in the Centre for Colloid Chemistry research group. The group is preparing a broad range of microphases (colloidal particles, nanoparticles) and functional (i.e. water repellent, self-cleaning, drug-storing and releasing), nanostructured thin film systems by wet colloidal chemical methods.

Colloidal particles carry great potential in many possible applications, and new areas are discovered and analysed every year. The importance of nanotechnology is underlined by the following data^{1,2}: between 2000 and 2015 the number of publications on nanotechnology increased from 19 754 to 141 663, and the global nanomaterials market was 10.89 billion USD in 2022, and it is expected to reach 32.77 billion USD by 2030.

An excellent example of cutting-edge research in nanotechnology is the production and characterisation of upconverting nanoparticles (UCNPs). My work was centred around this field.

The idea of upconversion emission being related to energy transfer between lanthanide ions came from F. Auzel in 1966³. Since then, the research work moved on from understanding the physical basis of said processes to utilising them in nanomaterials. Many synthesis methods were discovered, and the range of possible applications also broadened: the upconversion phenomenon could possibly be utilised among others in photodynamic cancer therapy^{4,5}, bio-imaging^{6,7}, light sources⁸, solar cell technology⁹, temperature sensing¹⁰, and photocatalysis¹¹.

The main aim of my research and development work was to study the emission properties of composite thin film systems containing NaYF₄ : Yb³⁺, Tm³⁺ upconverting nanoparticles in inorganic and biopolymer matrices. The preparation and characterisation of such nanocoatings can be beneficial in many of the above-mentioned potential applications of the upconversion phenomenon.

Energy transfer processes between fluorescent dye molecules and UCNPs are also part of the experimental work I conducted, studying the energy transfer interactions is also a crucial part of developing functional nanostructured coatings utilising upconversion photon emission.

In this paper, I will guide the Reader through the relevant scientific literature in the field of upconversion, then I will present my research and development work and its most promising results.

2 Literature review

2.1 The upconversion phenomenon

Photon upconversion explains photon emissions in which the energy of the emitted photon is higher than the energy of the excitation irradiation. The Stokes-shift observed in such emission has a negative value, thus an alternative name for these photon emissions is anti-Stokes emission. This phenomenon is observed among others in nanomaterials that are able to get consequentially excited by multiple photons, and then emit a single photon of higher energy.¹² Typically, upconverting nanoparticles emit photons in the UV and visible region of light after being excited by near-infrared radiation. See Figure 1 for a schematic overview of this process.

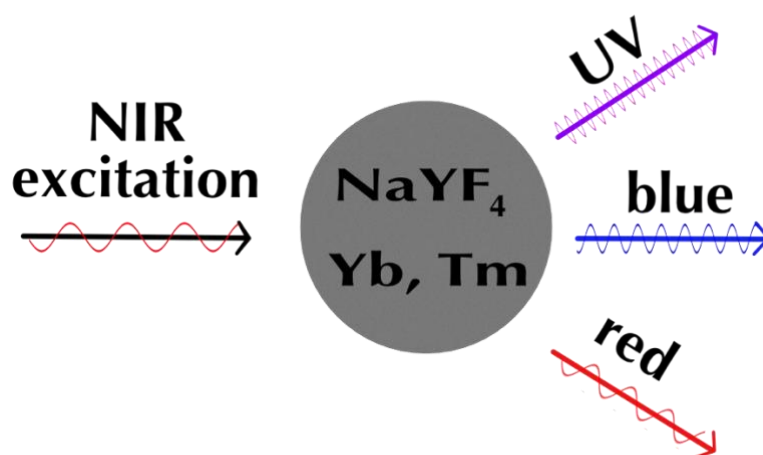


Figure 1. The upconversion phenomenon

Anti-Stokes emission can occur after various excitation and energy transfer steps between lanthanide dopant ions. Figure 2 demonstrates two of the most basic interactions. A possible mechanism for this phenomenon is energy transfer upconversion (ETU), which greatly demonstrates the need for different types of dopant ions. This mechanism is based on the ground state absorption (GSA) of two different kinds of lanthanide ions. After this initial absorption, the so-called sensitising ion transfers the absorbed energy to the activator ion. The excited electron of the sensitising ion relaxes to the ground state energy level and the already excited state electron of the activator ion undergoes further excitation. The energy transfer takes place via dipole-dipole interactions, which means that it requires the atomic orbitals of the participating ions to overlap. ETU is the most efficient upconversion mechanism.¹²

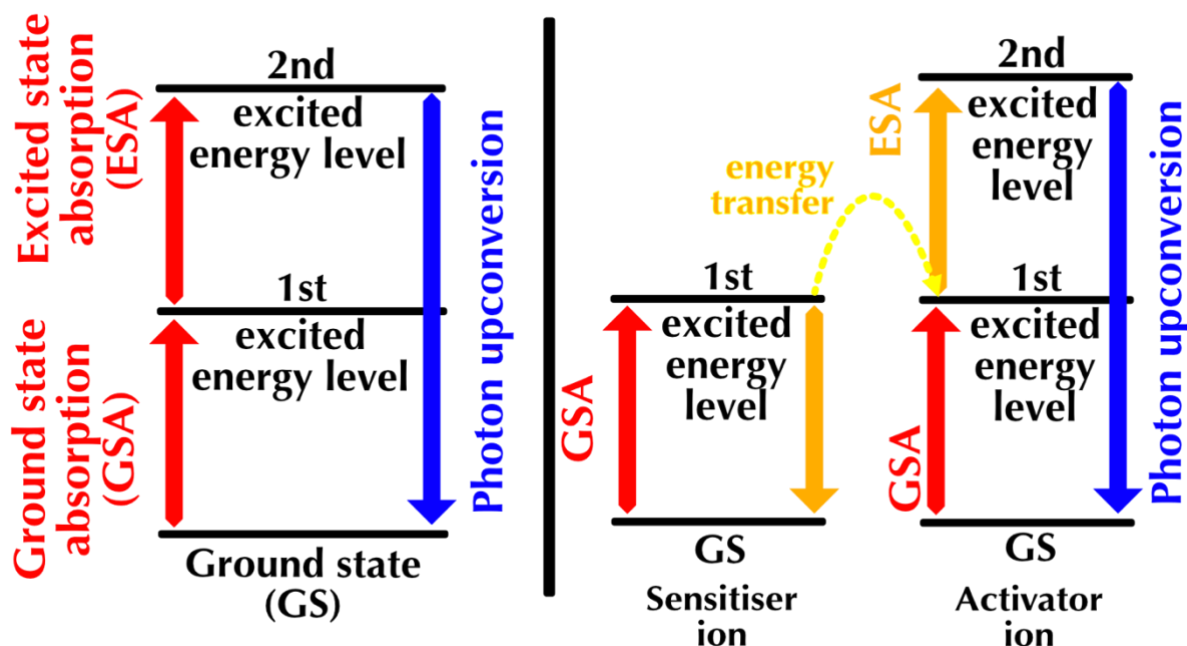


Figure 2. Selected mechanisms of upconversion photon emission (left: excited state absorption, right: energy transfer upconversion)

There are several potential uses for the upconversion phenomenon. The potential applications can be divided into two main parts: on the one hand, the visible or UV emission produced by low-energy NIR excitation can be exploited by another system (photodynamic therapy, solar cells, light sources), and on the other hand, monitoring changes in the intensity of the upconversion emission (pH¹³, temperature¹⁰) allows sensing applications. Another interesting use could be to utilise UCNPs as light sources. Several groups have reported intense, visible, white-coloured emissions. This was achieved by exciting different types of upconverting microphases side by side (colour tuning).^{8,14} There is also a military interest in UCNPs: NIR-to-Visible upconversion properties could be utilised in the area of NIR-detection in enhanced night vision goggles.¹⁵ Lanthanide-doped UCNPs can be especially suitable for anti-counterfeiting applications: the dopant rare earth ions possess many intermediate energy levels and distinguishable emission properties.¹⁶

2.2 Energy transfer processes between UCNPs and dye molecules

The energy transfer process between the upconverting colloidal particles and an organic compound, such as an organic fluorescent dye or a photosensitive drug carrier molecule, is crucial to a successful application. The study of this is of particular importance, as these radiative interactions form the basis of some specific applications.

V. Muhr and co-workers put dye molecules (e.g. Sulforhodamine B) onto the surface of upconverting nanoparticles. 980 nm laser excitation did not induce fluorescence of the dye molecules, but in a system where upconverting nanoparticles were also present, dye molecules were excited and exhibited fluorescence due to the anti-Stokes emissions of the upconverting nanoparticles. The donor in the energy transfer was the dopant ion showing anti-Stokes effect, whose green emission lifetime was selectively shortened. This proved that Förster resonant energy transfer (FRET) occurs between the two components. The acceptor was the fluorescent dye molecule. The energy transfer occurred between small distances through dipole-dipole interactions, without photon emission.¹⁷

B. Wu and co-workers have extended the excitability of SYBR green I DNA dye to the infrared region, using Förster resonant energy transfer from NIR-excited upconverting nanoparticles to dye molecules. The use of NIR excitation significantly reduced the amount of autofluorescence that interferes with the measured signals.¹⁸

Energy transfer can also occur from the excited dye molecule to the UCNP: X. Wang et al. and M. I. Saleh et al. have achieved Förster resonant energy transfer by excitation of NIR-emitting dye molecules. It was determined that the donor dye molecule must be very close to the nanoparticle surface, with a maximum distance of about 10 Å from which the FRET phenomenon occurs.^{19,20}

The area of drug delivery systems represents another energy transfer based potential application. The anti-Stokes emission of upconverting nanoparticles can be utilised inside the body: in photodynamic therapy, UV irradiation could be replaced by external NIR radiation that has no harmful effects on the body but is also deeply penetrating in tissues. By using appropriate surface ligands on the upconverting nanoparticles, photosensitive materials can be attached to the surface of microparticles, which undergo structural changes in response to NIR-induced anti-Stokes emission. Thus, the drug molecules attached to these photosensitive ligands are released into the body. In conclusion, the phenomenon of upconversion can be used for targeted photodynamic therapy.^{4,5,21} In photodynamic therapy, the aim is usually to kill cancer cells in a

targeted manner in the irradiated area.²² The irradiation induces upconversion photon emission inside the tissues: the temperature rise induced by said emission or the drug delivered by the carrier as a result of said emission causes the death of cancer cells. They can also serve as biological markers in imaging studies, following similar principles.^{6,7,18}

Biopolymer matrix coatings (chitosan²³ in my case) can serve as a good model medium for predicting processes in living tissues.

2.3 The structure and composition of upconverting nanoparticles

To achieve photon upconversion the nanomaterial is required to have a specific structure and composition. Upconverting nanoparticles consist of three major components: a difficult-to-excite, low phonon energy host lattice, which is doped with two different types of (usually) lanthanide ions. Typical lattices include NaYF₄, LaF₃, CaF₂, NaLuF₄ and Ba₂LaF₇.^{6,9,24,25,26} The dopants are categorised like this: there are sensitising ions that easily absorb NIR radiation and can efficiently transfer their excitation energy to a neighbouring dopant ion, namely the activator ion. The activator ion then relaxes from the multiply excited state via photon emission. Examples of the different required UCNP components are shown in Table 1.^{7,27}

Table 1. Types of dopant ions of upconverting nanoparticles

Activator ion	Sensitiser ion (with excitation wavelength)
Er ³⁺ , Tm ³⁺ , Ho ³⁺ , Eu ³⁺ , Mn ²⁺	Yb ³⁺ (980 nm), Nd ³⁺ (808 nm)

The quantum yield of upconversion emission is also dependent on the concentration of dopant ions, since at higher dopant contents other non-radiative relaxation pathways become more significant (vibrational relaxation, quenching).^{9,28,29} The lanthanide ions can only be doped in a narrow optimal concentration range. Typically, with a NaYF₄ lattice doped with ytterbium sensitising ion a concentration of 1.5...3% of erbium or 0.2...0.5% of thulium is required.^{12,30} With the combination of different dopant ions and different concentrations, the upconversion emission wavelengths and intensities can be tuned, for example, S. Sivakumar et al. developed a white light source using a combination of LaF₃: Yb³⁺, Tm³⁺; LaF₃: Yb³⁺, Er³⁺; and LaF₃: Yb³⁺, Eu³⁺.⁸

Lastly, the importance of organic capping agents must be discussed. If an environmental molecule with a readily excitable vibrational energy state comes near the surface of the upconverting nanoparticle, the probability of non-radiative relaxation increases, resulting in a decrease in upconversion photon emission intensity. To counter this surface passivation effect, various organic ligands are added to the nanoparticle suspensions. These ligands are then absorbed on the surface of UCNPs. Typical ligands include oleic acid, citric acid, poly(vinylpyrrolidone) (PVP) and poly(ethylene glycol) (PEG).^{31,32}

In my research work, PVP was utilised as an organic capping agent (Figure 3). This polymer provided dispersibility in ethanol and water, and actively prevented the non-radiative relaxation paths, thus maximising the achieved upconversion emission intensity.⁴

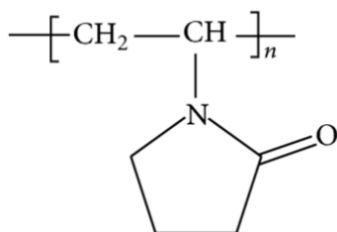


Figure 3. Molecular structure of PVP

2.4 The synthesis of upconverting nanoparticles

The most important aspects in the synthesis of nanoparticles include repeatability, tuneable particle size, optimal reaction time, and reaction conditions. The main challenge is the reliable, repeatable production of monodisperse (narrow size distribution) particles. The synthesis of upconverting nanoparticles requires solvents, which are usually organic compounds, so that during and/or after synthesis the surface of the microphases produced must be modified in order to make them dispersible in a polar medium.⁵ During the process, the desired nanoparticle is formed by a chemical reaction between the ions of the precursor, and the growth of the particles, the formation of the hydrophilic surface of said microphases (thus its dispersibility) is assisted by the added organic capping agents.^{7,33,34}

The three main methods most used for the synthesis of upconverting nanoparticles are the following: the thermal decomposition method, the co-precipitation method, and the hydro- and solvothermal synthesis³⁵. Thermal decomposition is one of the most used methods for the preparation of alkali lanthanide tetrafluoride nanoparticles (e.g. NaYF₄, NaGdF₄, NaLuF₄,

LiYF₄, and KGdF₄).^{29,36,37} Several research groups have been working on the optimisation of the co-precipitation method: NaGdF₄, NaTbF₄, CaF₂ and LaF₃-based upconverting nanoparticles have been successfully prepared.^{7,26,38,39} The thermal decomposition method is based on the thermolysis of different organometallic compounds using a high boiling solvent heated above the decomposition temperature of the organometallic precursors (> 300 °C). The co-precipitation reactions are faster, require less equipment and are simpler than the other two methods. Co-precipitation method was used to prepare the LaF₃ lattice UCNPs that were utilised in some of my experiments.²⁶ The solvothermal method is a size-, shape- and phase-controlled method for the preparation of monodisperse UCNPs, including lanthanide-doped NaYF₄. It requires lower temperatures than synthesis by thermal decomposition. In solvothermal syntheses, the precursor compounds are dissolved in a suitable solvent and the reaction between the reactants takes place at temperatures and pressures above the critical point of the solvent. The supercritical conditions must be provided to achieve the appropriate reaction rate and solubility. Due to the fluoride-containing precursors, an autoclave is required, usually thick, made of steel, hermetically sealed, with a protective coating (Teflon, titanium) on the inner surface to prevent corrosion.

2.5 The preparation of thin films containing UCNPs

For various practical applications, nanocoatings of upconverting nanoparticles are required. J. Park and co-workers fabricated a UCNP-containing perovskite solar cell by adding UCNP suspensions onto a poly(dimethylsiloxane) substrate and then removing the dispersing agent from the coating under vacuum. Further coatings required were then formed on the UCNP-containing substrate using spin-coating method.⁴⁰

M. F. Torresan and co-workers applied upconverting nanoparticles to a pre-treated glass substrate by spin-coating method, and then added a mesoporous metal oxide layer, also by spin-coating. The composite system was heat treated and the resulting system showed upconverting emission. The thin films were permeable due to their porosity. The authors' long-term goal is to develop temperature sensors using these coatings.⁴¹

In my work, I have tried a different way to fabricate composite coating systems: I will disperse the upconverting nanoparticles in the precursor sol of the chosen matrix material and then use these UCNP-containing sols in the composite coating forming process (spin-coating). I have not yet found such an approach in the scientific literature.

3 Aims

After reviewing the literature on upconversion, it has been made obvious that the scientific community still lacks knowledge on UCNP-containing composite thin films. However, sensing and photovoltaic applications could greatly benefit from results in this area. Accordingly, the main aim of our research is the development and characterisation of composite thin films of upconverting nanoparticles. We aim to test several matrix materials in the composite coating systems: silica as an inert matrix that could be useful in sensing applications; titania as a photoactive matrix material that could be utilised in self-cleaning, antibacterial surfaces and solar cell technology; and, finally, chitosan biopolymer as an environmental-friendly material that could also be used in future research to mimic the human tissue in model experiments in the biomedical field.

To prepare UCNP-containing thin film systems, the first step is to synthesize upconverting nanoparticles that show high upconversion emission intensities. A solvothermal method is used to synthesize NaYF₄: Yb³⁺, Tm³⁺ upconverting nanoparticles. After this, composite coatings with varying matrix materials are prepared via a spin-coating process. Our aim is to characterise and compare the upconversion emission properties of these composite thin film systems. One of the main areas of research and development of UCNPs is increasing the upconversion emission intensities.⁴² Keeping this goal in mind, the best available preparation parameters (composition, structure, deposition and post-treatment parameters etc.) are going to be determined for each matrix material, in order to achieve composite coatings with high upconversion emission intensities that are suitable for further studies.

Many of the above mentioned possible applications are based on energy transfer processes between the UCNPs and another material in the composite system. To characterise the energy transfer properties of the synthesized UCNPs model experiments need to be conducted using Rhodamine 6G fluorescent dye molecules both in UCNP suspensions and composite coatings of UCNPs. The dye concentration dependence of the energy transfer process is also of great importance.

4 Experimental

4.1 Materials, equipments and instruments used in this work

4.1.1 Materials

- Acetic acid (*Lachner*, 99.8% for analysis)
- Acetylacetone (*Acros Organics*, 99+%)
- Ammonia solution (*Lachner*, 25%)
- Ammonium fluoride (*Sigma Aldrich*, 99.99%)
- Chitosan (*Sigma-Aldrich*, medium molecular weight, viscosity: 598 cps)
- Erbium(III) chloride hexahydrate (*Sigma Aldrich*, 99.9%)
- Ethanol (*Emplura*, 98%)
- Ethylene glycol (*Lachner*, 99.6%)
- Glass substrate (*Menzel-Gläser*, 76 x 26 mm microscope slide)
- Hydrochloric acid (*Carlo Erba*, 37% for analysis)
- Isopropyl alcohol (*Reanal Labor*, 99.7%, for analysis)
- Lanthanum trifluoride: 4% ytterbium, 0.1% thulium UCNPs ($\text{La}_{0.959}\text{Yb}_{0.04}\text{Tm}_{0.001}\text{F}_3$, *Holikem Ltd.*)
- Pluronic® P-123 PEG-PPG-PEG triblock copolymer (*Sigma Aldrich*, M- 5800 g/mol)
- Poly(vinylpyrrolidone) (*Sigma Aldrich*, K-30, $M_{\text{av}} = 40\,000$ g/mol)
- Rhodamine 6G (*Sigma Aldrich*, 95%)
- Sodium chloride (*Sigma Aldrich*, 99.9%)
- Sulphuric acid (*Carlo Erba*, 96%, for analysis)
- Tetraethyl orthosilicate (*Acros Organics*, 98%)
- Thulium(III) chloride hexahydrate (*Sigma Aldrich*, 99.9%)
- Titanium (IV) isopropoxide (*Acros Organics*, 98+%)

- “Ultra” dishwashing powder (*DunaChem Ltd.*)
- Ultrapure water (Specific resistance: 18.2 MΩcm, TOC: 7 ppb, *Adrona Integrity+*)
- Ytterbium(III) chloride hexahydrate (*Sigma Aldrich*, 99.9%)

4.1.2 Equipments

- Analytical laboratory balance (*Kern ABJ 120-4NM*)
- Autoclave (stainless steel, volume: 100 cm³)
- Automatic pipette (*Artorius Biohit*, *Biohit Proline*, *Jencons Sealpette*)
- Balance (*Sartorius L 2200 P*)
- Centrifuge (*HERMLE Z 36 HK*)
- Drying cabinet (*Memmert BASIC*)
- Furnace (*Nabertherm Controller B 170*)
- Glass electrode pH meter (*Adwa Ad 11*)
- Magnetic stirrer (*IKA*) and stirrer bar
- NIR Laser pointer (980 nm, < 50 mW power)
- Spin-coater (*Specialty Coating Systems 6800 Spin Coater Series*)
- Ultrasonic bath (*Simex*, *Elma*, *S 15 H Elmasonic*)
- Vortex machine (*FALC*)
- Water purification system (*Adrona Integrity+*)
- Glassware, porcelainware, Teflon beakers, centrifuge tubes, spatulas, tweezers

4.1.3 Instruments

- Camera (*Nikon COOLPIX 995*)
- Ellipsometer (*Semilab Sopra EP-12*)

- Optical microscope (*Carl Zeiss Jena*)
- Spectrofluorometer (*Edinburgh Instruments Spectrofluorometer FS5*)
equipped with 980 nm NIR CW laser (*Edinburgh Instruments MDL-III-980-2W*)
- UV-Vis spectrophotometer (*Analytik Jena Specord 200*)
- X-ray diffractometer (*Philips Analytical X'Pert Pro*)

4.2 Preparation of samples

Disclaimer: I have synthesized Tm-doped NaYF₄ lattice upconverting nanoparticles, but I will also present results obtained with Tm-doped LaF₃ lattice UCNPs prepared by one of our partners (Gyula Tolnai, Holikem Ltd.). The LaF₃-based UCNPs were synthesized via co-precipitation method.²⁶

4.2.1 Synthesis of UCNPs by a solvothermal method

Based on previous work of the Centre for Colloid Chemistry research group, I prepared Yb- and Tm-doped NaYF₄ lattice upconverting nanoparticles via solvothermal method. The precursors of the synthesis were inorganic salts (chlorides) of the required rare earth elements. The optimal dopant content – in case of emission intensity – was 0.5 molar% of thulium and 20 molar% of ytterbium. Ethylene glycol was used as solvent and poly(vinylpyrrolidone) (PVP, $M_{av}=40\,000$ g/mol) as an organic capping agent.

The inorganic salts and PVP were solved in ethylene glycol in Teflon beakers and then stirred at 80 °C. The reaction mixture was transferred to a stainless steel autoclave and it was finally heated to 200 °C (in 35 minutes), then kept at that temperature for 12 hours. The autoclave was 50 % filled. The required amount of precursor materials can be seen in Table 2. The reaction equation was the following:

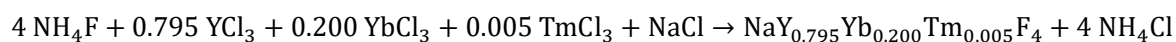
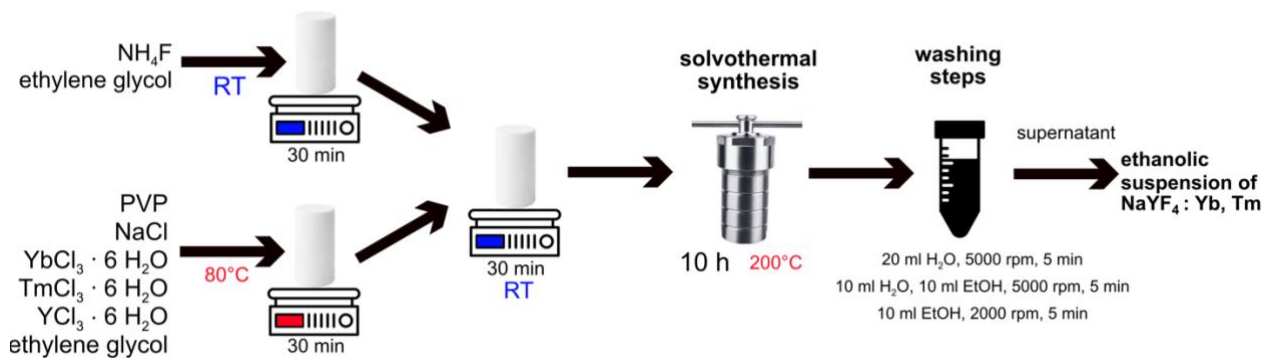


Table 2. Required amount of reagents for the solvothermal synthesis

material	mass [g]
NaCl	0.2104
PVP ($M_{av}=40\,000$ g/mol)	1.2826
$\text{YbCl}_3 \cdot 6 \text{H}_2\text{O}$	0.1395
$\text{TmCl}_3 \cdot 6 \text{H}_2\text{O}$	0.0035*
$\text{YCl}_3 \cdot 6 \text{H}_2\text{O}$	0.4341
NH_4F	0.2104

* 0.0300 g $\text{TmCl}_3 \cdot 6 \text{H}_2\text{O}$ dissolved in 5,00 mL of ethylene glycol at 80 °C, using 575 μL of said solution.

After cooling down to room temperature, the product was separated into two centrifuge tubes and washed with 20-20 mL of distilled water and ethanol by several centrifugation steps (*HERMLE Z 36 HK*, 5000 rpm, 5 min). In the final washing step, the synthesis product was recollected in a single centrifuge tube along with 20 mL of ethanol. A lower rotational speed of 2000 rpm was used in this final step to separate the nanoparticles in the desired size range from the greater grain-sized fraction. The supernatant after the centrifugation was a kinetically stable ethanolic suspension of upconverting nanoparticles. This suspension was later used in the preparation of composite coatings. Five minutes of stirring in ultrasonic bath was carried out every time before the preparation of the coating precursors. A scheme for the entire synthesis process can be seen in Figure 4.

**Figure 4.** Scheme of the solvothermal synthesis

The solid microphase content of these suspensions was measured. 0.500 mL of the ethanolic suspension was dispensed into a porcelain bowl with known mass (0.1 mg accuracy). The dispersing agent (ethanol in this case) was then vapourised at room temperature. The mass of the remaining solid phase was calculated after achieving a constant mass.

4.2.2 Heat treatment of the synthesized UCNPs

We will see in Chapter 4.2.3 that during the preparation of composite thin film systems, in many cases a heat treatment step is required. To see the effect of heat treatment on the emission properties of upconverting nanoparticles used to create the coatings, UCNP powders were also annealed in the same way as their coatings would be. It is important to note that the NaYF₄: Yb, Tm UCNPs used in later preparative work were not heat treated before the coating process.

To prepare the afore-mentioned powders, UCNP suspensions were dried at 70 °C. About 20 mg of the as-obtained nanoparticle powders were heat treated in the same way the coatings would be annealed: at 120 °C for 10 hours (after 20 mins of heating) and at 450 °C for 30 mins (after 20 mins of heating). The resulting heat-treated powders were later characterised by XRD. These were then redispersed in ethanol and the fluorescence emission properties were measured.

4.2.3 Preparation of thin film systems

The Centre for Colloid Chemistry has significant experience in the field of thin film preparation using sol-gel method. In the sol-gel coating process, the volatile component of the precursor sol (ethanol or water in my case) evaporates during the coating formation, which leads to gelation of the coating (formation of a liogel coating). The final step is conditioning (annealing). During conditioning, excess liquid evaporates, further chemical processes take place, the structure stabilises, and a three-dimensional continuous oxide space network is formed (xerogel coating).^{43,44,45} Nano-structured coatings are being prepared via Langmuir-Blodgett, dip-coating, and spin-coating techniques in the research group. For my research work, due to the small amount of available nanoparticles, the spin-coating process is most beneficial. In this method, a droplet of sol is placed at the centre of a spinning substrate, and the thickness of the resulting film can be varied with rotational speed, temperature, viscosity, and solid phase content. A schematic overview of the spin-coating process can be seen in Figure 5.

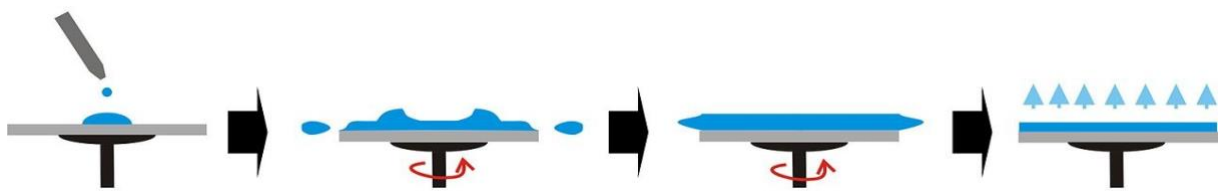


Figure 5. The spin-coating process⁴⁶

Upconverting nanoparticle containing composite coatings consisting of compact silica, mesoporous titania, and chitosan biopolymer matrix material were prepared via spin-coating method on a glass substrate. Some chitosan matrix samples were also deposited on silicon wafers for ellipsometry measurements. The synthesis of precursor sols was carried out via acid-catalysed hydrolysis and polycondensation mechanism from silicon- and titanium-alkoxide reagents. This method was similar to that reported previously by our research group.^{47,48}

A summary of the prepared samples can be seen in Figure 6 and Table 3.

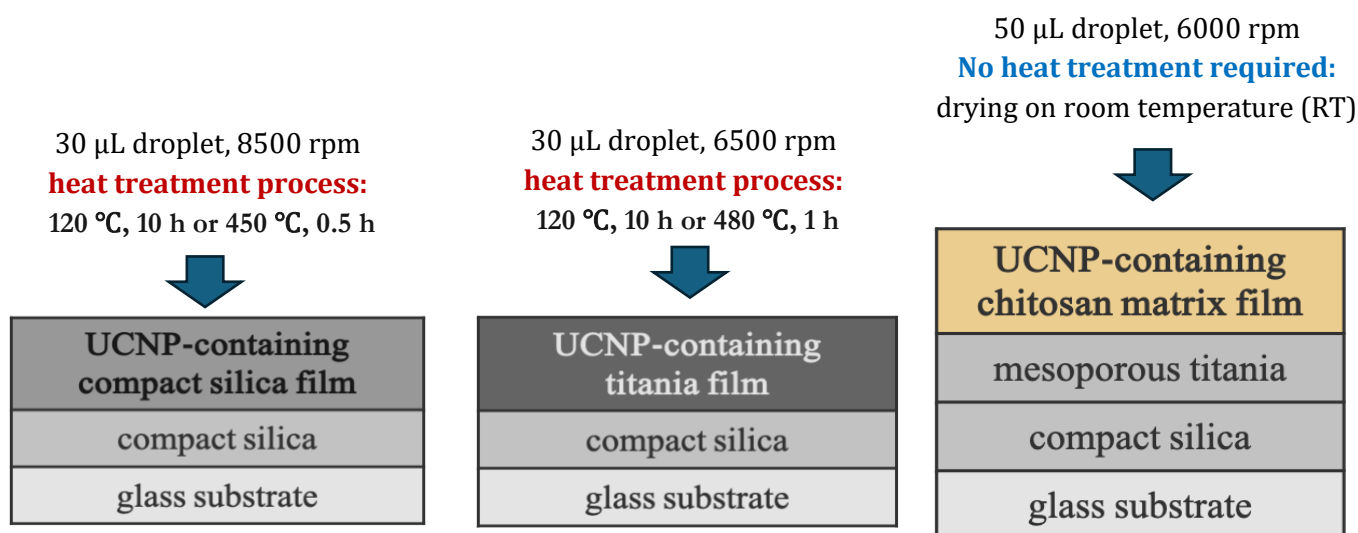


Figure 6. The structure of the prepared composite coatings of upconverting nanoparticles

Table 3. Summary of the prepared composite coatings

Type of coating	SiO ₂ protective layer	undoped TiO ₂ layer	matrix material of composite UCNP-coating	heat- treatment needed
SiO ₂ /UCNP	yes	no	silica	yes
TiO ₂ /UCNP	yes	no	titania	yes
chitosan/UCNP	yes	yes	chitosan	no
glass/UCNP	no	no	air	no

Synthesis of precursor sols.

The silica precursor sol was prepared by adding 10 mL of hydrochloric acid (with a concentration of 0.1 M) to 38.5 mL of ethanol. To this 31 mL of tetraethyl orthosilicate (TEOS) was added and the mixture was stirred at room temperature for one hour until hydrolysis and polycondensation reactions took place. The sol was left to rest overnight at 25°C. A graduated cylinder was used to measure the volume of the liquids.

As for the titania precursor sol, 2.50 g of Pluronic P-123 copolymer was weighed on an analytical balance and dissolved in 25 mL ethanol at room temperature in a covered beaker with constant stirring. Then 3.75 mL of Ti(IV) isopropoxide was pipetted into the solution and 1.25 mL of acetylacetone was added drop by drop. Stirring was continued for 1 hour at room temperature and the sol was stored at 25 °C until use. The sol was used for coating preparation the next day.

In case of chitosan matrix thin films, the coatings were prepared from a 1% aqueous solution of chitosan. To create the solution, I weighed 49.0 g of ultrapure water and pipetted 0.500 mL of acetic acid. Then, 0.500 g of chitosan was added to the solution on an analytical balance and the solution was stirred at room temperature for 24 hours. Afterwards, the insoluble contaminants were removed via centrifugation at 4000 rpm rotational speed for 30 min, and then the resulting supernatant was used to create the UCNP suspension from which the composite coatings were prepared.

Pre-treatment of the substrate:

The substrate used for most coatings was a thoroughly cleaned microscope slide glass. The following chemicals were used for cleaning the glass surface: *Ultra* powder, 10 w/w % sulphuric acid solution, isopropanol, and ultrapure water. Initially, I cut the microscope slides in half. The resulting glass slides were first dipped in a solution of *Ultra* powder and then rinsed with ultrapure water. In this step, I tried to remove the additives and contaminants used in glass production from the glass surface. I then wiped the glass sheets dry with a paper towel and repeated the previous steps with the sulphuric acid solution. At this point, the surface hydroxyl groups were protonated. I then wiped the glass plates with an isopropanol-containing cotton wool, rinsed with isopropanol and finally with ultrapure water. As a last step, I placed the cleaned glass supports in a drying cabinet at 70 °C.

A compact silica coating was applied to the surface of the pre-cleaned glass substrate in all cases. This prevented the highly mobile sodium ions present in regular glass from affecting the composition of the thin films that were later formed. The name compact refers to the fact that the produced layer is of very low porosity (at most microporous).^{43,44} In some of my samples, the compact silica coating not only had a protective function but served as a matrix material for the composite coatings (see later).

Preparation of the composite coating systems:

The UCNPs were dispersed in the different precursor sols using the following method: Ethanolic suspensions of known UCNP content were centrifuged (5000 rpm, 5 min), then the remaining nanoparticle precipitate was redispersed in the precursor sols via vortex machine and ultrasonic bath. The UCNP content of the resulting suspension was 5, 10 or 20 mg/mL.

The coating process was carried out using a Specialty Coating Systems 6800 Spin Coater Series device. 30 µL droplet and 8500 rpm speed were used for the silica films, 30 µL droplet and 6500 rpm speed for titania, and 50 µL droplet and 7000 rpm for chitosan matrix coatings. The time of acceleration was 20 s, the duration of spinning at the required rate was 1 min, and the deceleration took 5 s. 1...3 UCNP-containing layers were deposited on the substrates. Around five minutes passed between the formation of the next layer in case of multi-layered coatings. This left time for the initial drying of the films. Some double-sided samples were also created:

This means that after the completion of 3 consecutive layers of chitosan matrix composite coatings, 3 additional layers were applied to the other side of the pre-treated glass substrate.

To achieve the final stabilised structure of the xerogel coatings an annealing process was needed for the silica and titania matrix films.

The coating process is a sol-gel method, meaning that the precursor sol becomes a liogel (gel with high liquid content) which then turns into a xerogel (gel with minimal liquid content) via a drying process.^{43,44,45} Two heat treatment methods were applied: The samples were placed in a furnace (*Nabertherm B170*) for heat treatment at either 120 °C for 10 h (SiO_2 and TiO_2 coatings) or 480 °C for 1 h (TiO_2 coatings), and 450 °C for 30 min (SiO_2 coatings). The heat treatment parameters were chosen to reach suitable stability and avoid significant shrinkage of the coatings. Some silica and titania matrix coatings were dried at room temperature (RT) to study the effect of heat treatment on the structure and emission properties of the composite thin films. In the case of chitosan matrix composite coatings an atmospheric, room-temperature drying step was enough to achieve great stability (annealing is not needed, nor would it be possible in the case of biopolymer films).

A scheme for the composite coating preparation can be seen in Figure 7.

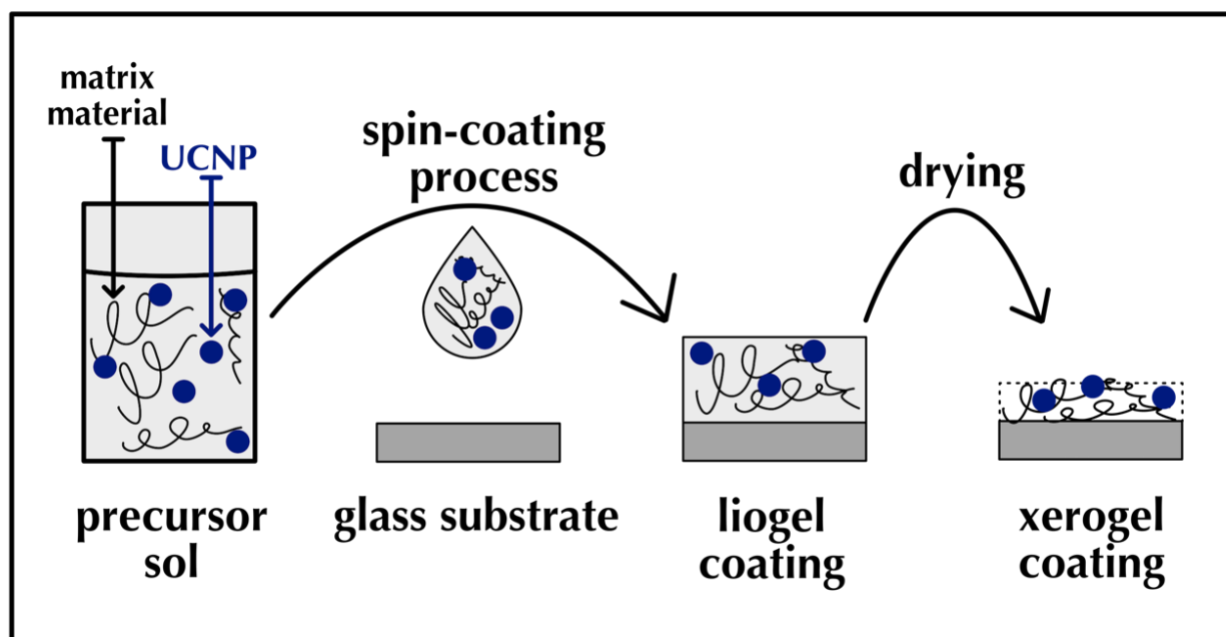


Figure 7. Scheme for the preparation of composite thin films of upconverting nanoparticles

I also tried to prepare coatings using the initial ethanolic UCNP suspensions. Spin-coating method was used. 30 μL of UCNP suspension was added to a spinning substrate that already contained a silica protective layer and a titania coating. I used the same spin-coating parameters as for the chitosan matrix films.

Finally, the order of layers for the composite coatings with varying matrix material was the following: a protective silica layer was formed in every case. For the silica matrix films, the next layer was the UCNP-containing silica coating. As for the titania matrix films, the composite titania matrix film of upconverting nanoparticles was formed on top of the compact silica layer. Finally, for the chitosan matrix composite thin films the composite UCNP-containing layer was formed on top of a substrate that already was silica and titania coated.

4.3 Characterisation of suspensions and coatings of UCNPs

The upconversion emission properties of the microphases prepared were characterised by spectrofluorometric analysis of their suspension. This method is also suitable for the characterisation of composite coatings containing upconverting particles after the replacement of the sample holder. It is also important to characterise the optical properties of the thin films produced, which can be investigated by UV/Vis spectrophotometry or ellipsometry. Questions that arise during annealing can be answered by X-ray diffraction. These methods are described in the next section of this report.

4.3.1 UV/Vis spectroscopy and optical microscopy

An ethanolic suspension of 1 mg/mL UCNP content was prepared by dilution of initial suspension, and the absorbance spectra were recorded using a UV-Vis spectrophotometer. Pure ethanol was used as a reference and the spectra were recorded in a quartz cuvette with a path length of 1 cm, wavelength range 350...1100 nm, 1 nm step size and scanning rate 10 nm/s.

The transmittance spectra of the glass substrates and the samples after the formation of the individual layers, which were also heat treated, were also recorded with a UV-Vis spectrophotometer. Parameters were set to 1 nm step size, 10 nm/s scanning speed. The reference was air. The transmittance spectra were recorded in the visible range, 350...1100 nm.

Some silica coatings showed a cracked, opaque surface after the heat treatment process and it could be assumed that they contain inhomogeneities on the microscopic scale (μm magnitude). The structure of these coatings was analysed via optical microscopy (*Carl Zeiss Jena*) using a 40x objective and microscopic images were recorded with an external camera (*Nikon COOLPIX 995*) connected to the microscope.

4.3.2 Fluorescence spectroscopy

Characterisation of suspensions: Upconversion photon emission intensities were studied by fluorescence spectroscopy (Edinburgh Instruments Spectrofluorometer FS5), using a 980 nm monochromatic continuous wave (CW) laser light source for excitation. Due to the sensitivity of the detectors and the increased light scattering of the suspensions, an ethanolic suspension diluted to 1 mg/mL UCNP was prepared. The emission spectra of said 1 mg/mL ethanolic suspensions of the UCNPs were measured in a quartz cuvette kept at 20.0 °C, in a range from 300 to 700 nm wavelength, with 1 nm step size, 0.5 s dwell time, 1.85 nm scan slit, and laser power of 1.49 W. By controlling the slit width, we are able to influence the number of photons that reach the detector.

Different particles emit at different intensities, so to stay within the measurement limit of the detector and not damage it, the slit width needs to be varied from sample to sample. The spectra of different suspensions can be compared for a given instrument when the exact same parameters are set for both measurements.

Characterisation of thin films: The upconversion emission properties of the model composite coatings were also analysed using a spectrofluorometer. The parameters of the measurements were the same as before, only the slit size needed an adjustment to 4.5 nm, due to the different nature of samples and altered geometry of the sample holder cells. The fluorometric measurement was carried out in a similar way as for the suspensions.

Characterisation of energy transfer processes: To characterise the energy transfer process between UCNPs and fluorescence organic dye molecules a quartz cuvette was filled with ethanolic UCNP-containing Rhodamine 6G (R6G) dye solution or a UCNP-containing chitosan film was placed in the cuvette and this system was filled with pure dye solution.

Thus, the coating became immersed in a fluorescence dye solution. The concentration of the dye varied from sample to sample (0...20 μM in case of suspensions and 0...100 μM for composite coatings), the UCNP content was kept constant in all cases. The fluorescence spectroscopy measurements were carried out using the same method and parameters as stated before.

To measure coatings in a cuvette containing dye solution, I had to cut the thin film samples lengthwise into 3 equal parts (1.1...1.2 cm). I measured the middle part of the original sample which I placed in the cuvette at an angle of about 45°. The measurement setup is shown in Figure 8.

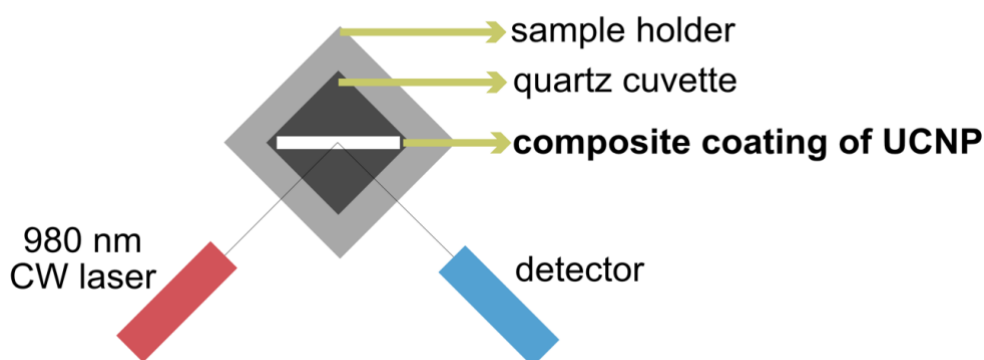


Figure 8. The placement of coating in a cuvette for spectrfloourometric measurements

4.3.4 X-ray powder diffraction

X-ray diffraction measurements were performed on powder samples of NaYF_4 : 20% Yb^{3+} , 0.5% Tm^{3+} microphases. I also recorded diffractograms of powders heat-treated at 120 °C and 450 °C.

A small amount of the powders was placed on a silicon wafer, which was then placed in the instrument so that the X-ray beam ($\text{Cu K}\alpha_1 = 0.154178 \text{ nm}$) hit the sample. A measuring voltage of 40 kV and 30 mA was applied. The angular range of the measurement was 4...84°, the step size was 0.0167° and the scanning rate was 5 seconds/step.

4.3.5 Ellipsometric Porosimetry

Ellipsometric Porosimetry (EP) measurements were carried out by *Semilab's PS-2000* apparatus. During EP the measurement, vapour (e.g. water or toluene vapour) adsorption in the pore structure of a thin film can be studied step by step through spectroscopic ellipsometry. It is a technique capable of the characterisation of porous thin films: refractive index, film thickness, open porosity, pore size distribution, surface area, and mechanical strength can be obtained as a result. During the measurement vapor of the adsorptive material condenses in the pore system which induces effective refractive index shift. UCNP-containing and UCNP-free chitosan coatings were deposited onto Si wafer substrates. The adsorption and desorption isotherms were taken at 24 °C, using ultra-pure distilled water as adsorptive material. The measurement was carried out in the 173.6...971.5 nm wavelength range at a 60° angle. Refractive index and film thickness at zero relative pressure were calculated using the Cauchy model via *Semilab Ltd. SEA* software.

5 Results and discussion

The structure of this part of my report is the following: first, I will highlight my results obtained through microstructural investigation methods (optical microscopy, transmission electron microscopy, X-ray diffraction), then I will detail the results of the fluorescence spectroscopy measurements, which is the core measuring method of my research work. The results obtained from suspensions and composite coatings are presented in two different sections. Finally, I will explain my results around energy transfer process characterisation.

5.1 Structural characterisation of the microphases

A transmission electron microscopy image and the calculated size distribution of NaYF₄: 20% Yb, 0.5% Tm nanoparticles is shown in Figure 9.

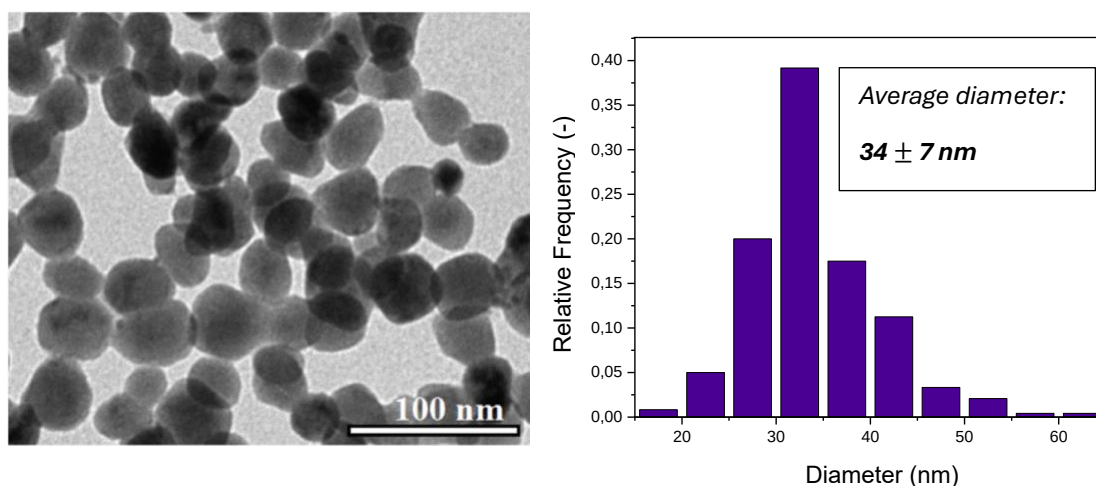


Figure 9. TEM image (left) and size distribution (right) of NaYF₄: 20% Yb, 0.5% Tm UCNP

The result of the solid microphase content measurement was (15.3 ± 0.6) mg/mL and (13 ± 1) mg/mL in two separate syntheses. The suspensions had to be diluted up to 1 mg/mL for fluorescence spectroscopic measurements.

The mass change of the annealed UCNP powders was also measured. The mass reduction after the heat treatment at 120 °C was negligible, while for the 450 °C annealing, a 9% mass loss was observed. This is probably due to the degradation of the organic capping agent (PVP). Furthermore, the powder sample may still contain trace amounts of ethanol or water from air humidity: the removal of these at elevated temperatures may also contribute to the change in weight.

The X-ray diffractograms of the heat-treated and untreated NaYF₄: Yb, Tm samples are shown in Figure 10. The crystal phase of the synthesised nanoparticles was cubic (α) according to the database (see Figure 10. left side). There was no change in crystal phase after annealing (see Figure 10. right side).

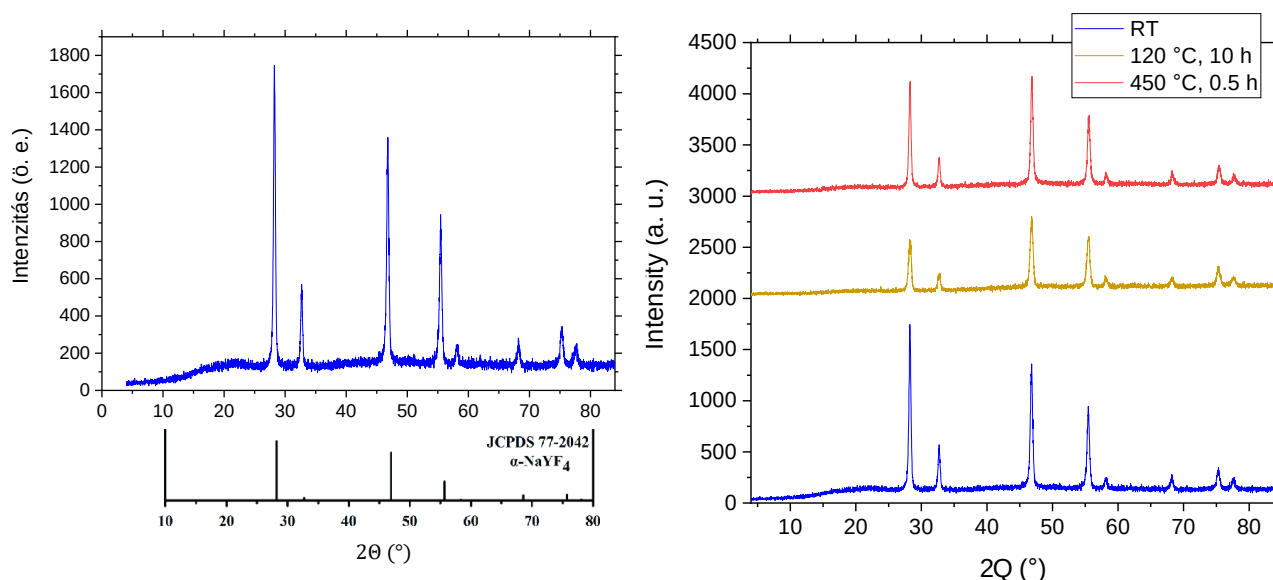


Figure 10. X-Ray diffractogram of NaYF₄: 20% Yb, 0.5% Tm UCNPs powder (left) and annealed UCNPs powders of the same nanoparticles (right); RT (room temperature) represents the samples that were not heat-treated.

From the diffractograms, the crystallite size can be estimated using the Scherrer equation:

$$\tau = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$$

where τ [nm] is the average crystallite size, $K = 0,94$ [-] is a constant (assuming spherical geometry), λ [nm] is the wavelength of irradiation, β [rad] is the half-width for a given peak, and θ [rad] is the diffraction angle for this said peak.

The calculations were performed for the peak at 28.2°. The results are summarised in Table 4.

Table 4. Crystallite size of annealed and untreated NaYF₄: 20% Yb, 0.5% Tm UCNPs

	untreated	annealed at 120 °C	annealed at 450°C
α -NaYF ₄ : Yb, Tm	25.6 nm	18.8 nm	25.5 nm

Heat treatment at a lower temperature resulted in a decrease in crystallite size, but at higher temperatures, the calculated value was approximately the same as the initial value. The effect of heat treatment is rather complex in case of nanoparticles (due to their high surface areas), as volatile components (ethanol, bound water) remain present in the final product from the synthesis step. These components are then capable of causing structural changes.⁴⁹ The reduction of the initial crystallite size is surprising at first, but similar results can be observed in other types of upconversion systems.⁵⁰

Finally, the transmission electron-microscopic image and the size distribution of the LaF_3 : Yb, Tm nanoparticles are shown in Figure 11. These upconverting nanoparticles are also going to be present in some coatings later, thus their discussion in this section is also crucial.

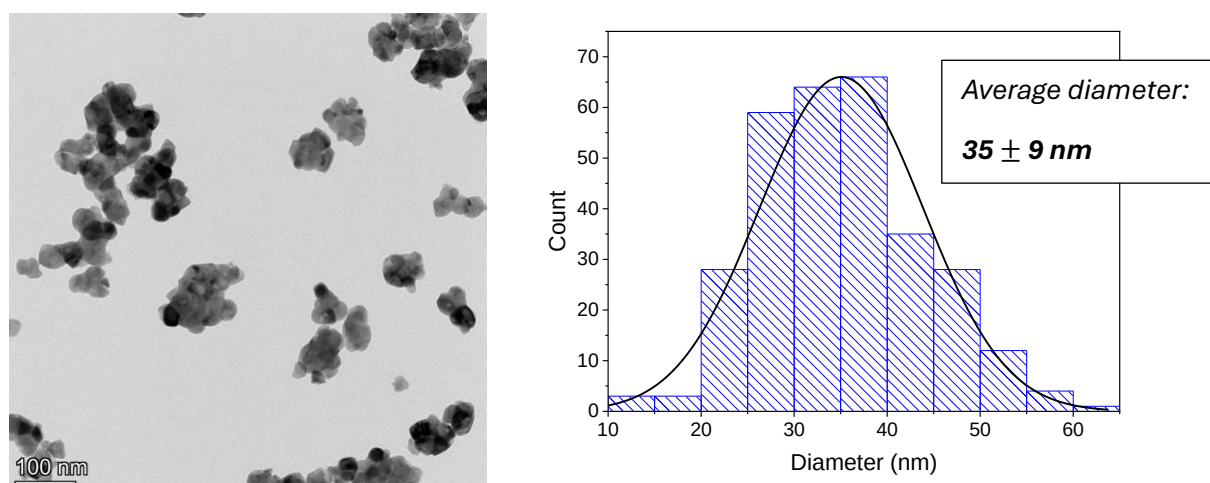


Figure 11. TEM image (left) and size distribution (right) of LaF_3 : 4% Yb, 0.1% Tm UCNPs

5.2 Emission properties of UCNP suspensions

Upconverting nanoparticles containing Yb^{3+} as a sensitising ion can be excited under 980 nm wavelength NIR irradiation.¹² The absorbance spectrum of 1 mg/mL ethanolic NaYF_4 : Yb, Tm UCNP suspension proves this, the spectrum can be seen in Figure 12.

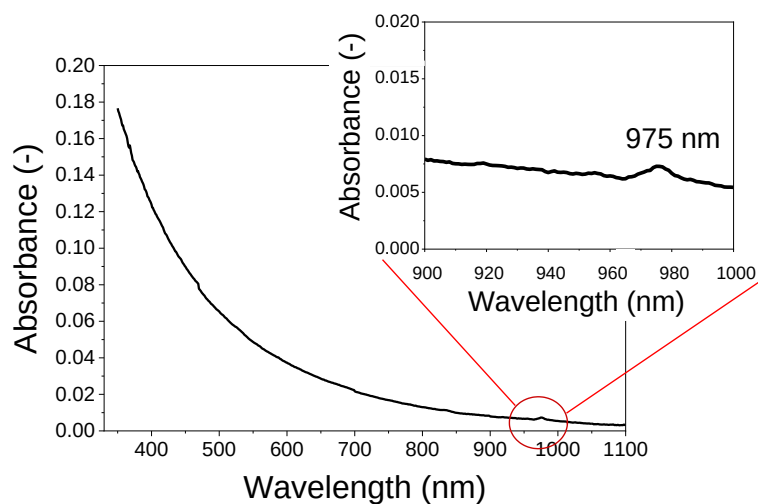


Figure 12. Absorbance spectrum of 1 mg/mL ethanolic UCNPs-suspension (NaYF₄: 20% Yb, 0.5% Tm)

The fluorescence emission spectrum with the corresponding energy level transitions of ethanolic 1 mg/mL NaYF₄: Yb, Tm upconverting nanoparticle suspension is shown in Figure 13. The energy level transitions coincide with those reported in the literature.

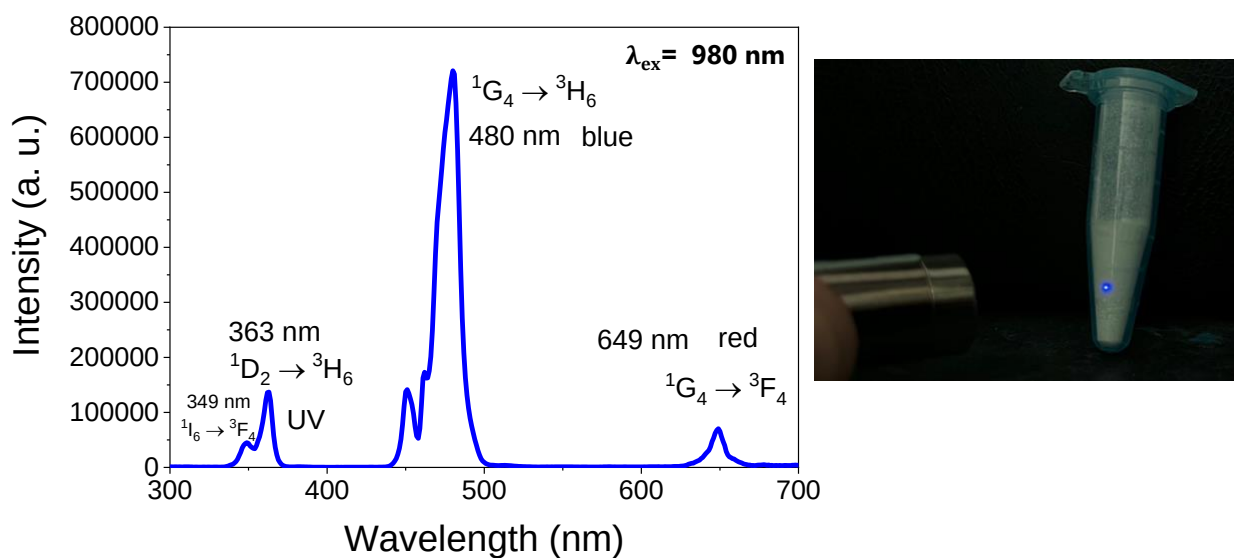


Figure 13. Emission spectrum of 1 mg/mL ethanolic NaYF₄: 20% Yb, 0.5% Tm UCNPs suspension (left) and an image demonstrating the upconversion phenomenon using a NIR laser pointer and a powder sample of the same UCNPs (right).

The emission spectra of 1 mg/mL ethanolic suspensions prepared from heat-treated NaYF₄: Yb, Tm UCNPs can be seen in Figure 14. It is noticeable that after 120 °C heat treatment, the emission intensities of the UCNP suspension are nearly the same as the untreated suspension. However, annealing at 450 °C resulted in a significant decrease in emission intensity. This may be a result of the degradation of the organic capping agent. Due to this degradation the probability of non-radiative emissions increases resulting in a decrease in fluorescence emission intensity. Moreover, other structural changes may occur in the nanoparticles as a result of heat treatment: for example, dopant ions may segregate into separate particles, which also results in reduced emission intensity.²⁶ Further experiments would be needed to establish a certain cause for the observed phenomenon.

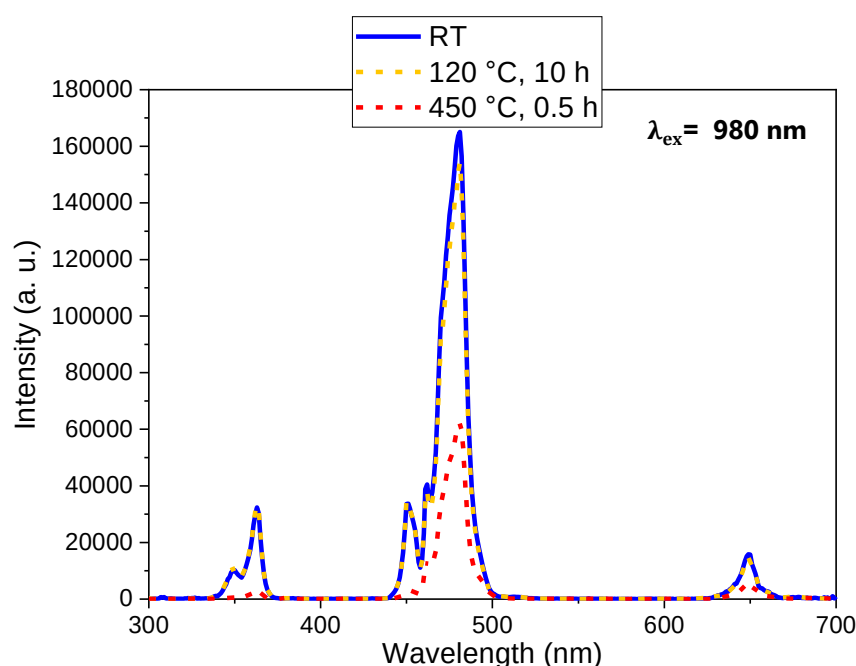


Figure 14. Emission spectra of 1 mg/mL ethanolic suspensions of annealed and untreated NaYF₄: 20% Yb, 0.5% Tm UCNPs

Lastly, I would like to present the emission spectrum of the 1 mg/mL ethanolic suspension of LaF₃: Yb, Tm upconverting nanoparticles²⁶. The emission peaks are characteristic to the dopant ions, thus the emission peaks can be measured at the same wavelengths as in case of NaYF₄ lattice UCNPs (Figure 15).

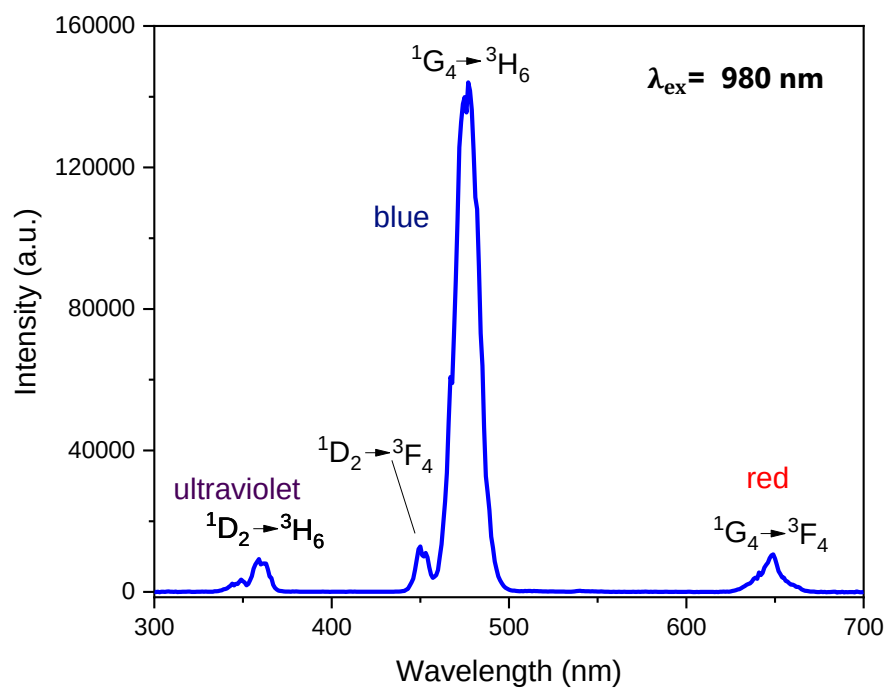


Figure 15. Emission spectra of 1 mg/mL ethanolic suspension of LaF₃: 4% Yb, 0.1% Tm UCNP

5.3 Structural characterization of composite coatings

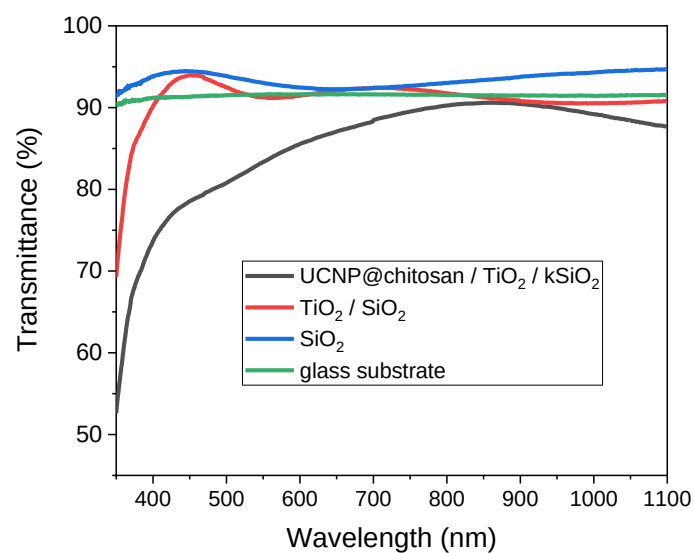


Figure 16. Transmittance spectra of the different prepared thin films (silica, titania and chitosan-based coatings)

Figure 16 shows a diagram of the transmittance spectrum of different types of coatings on glass substrates.

It can be observed that as more layers were deposited onto the glass substrate, the higher number of local maximum and minimum places on the curves could be observed due to the increased thickness. The only exception is coatings that include colloidal particles with upconverting properties, particles in the colloidal size range show significant light scattering, resulting in a decrease in transmittance. This effect is more significant at shorter wavelengths.

Thin-film optical model fitting^{51,52} was performed on silica^{43,44} and titania⁴⁷ coatings containing no UCNPs (the model cannot be used for samples that show significant light scattering, because of this, composite coatings containing UCNPs were not analysed with this method). The values of average coating thickness (d / nm), refractive index (n / -) and porosity (ε / %) were obtained as a result of the fitting. The results are summarized in Table 5. The exact procedure for thin film optical fitting is described in the Appendix.

Table 5. The results of thin film optical fitting on different types of coatings

Type of coating	mesoporous TiO ₂ coating			compact SiO ₂ coating	
	n [-]	d [nm]	ε [%]	n [-]	d [nm]
SiO ₂	-	-	-	$1.438 \pm 0,007$	190 ± 9
TiO ₂	$1.609 \pm 0,009$	78 ± 4	46 ± 1	$1.454 \pm 0,007$	178 ± 12

The refractive index of the compact silica layers is very close to the literature refractive index (1.462)⁵³, which shows that a non-porous (or slightly microporous) thin layer has been formed. The thickness of the coating is about 200 nm: the coating has a protective function, a thick protective layer of around 200 nm is already sufficient to significantly inhibit the diffusion of Na⁺ ions from the glass into the titanium dioxide coating. The mesoporous titanium dioxide coating formed by the templating method had high porosity according to the fitting results. Furthermore, it is an important finding that the thickness of the protective silica layer was reduced in the case of the two-layer coating. This layer shrank due to the sample undergoing another heat treatment after the titania coating was applied.

Figure 17 (top side) shows the transmittance spectra of compact silica matrix thin films after different heat treatments or a drying step at room temperature. The heat-treated coatings are thinner, as the number of minimums and maximums in the spectra is reduced after heat treatment. This means that the heat treatment has caused the layers to shrink. Furthermore, in case of the compact silica matrix material, the light scattering effect was more dominant in the case of the heat-treated coatings, which was also visible with the naked eye, the coatings were opalescent.

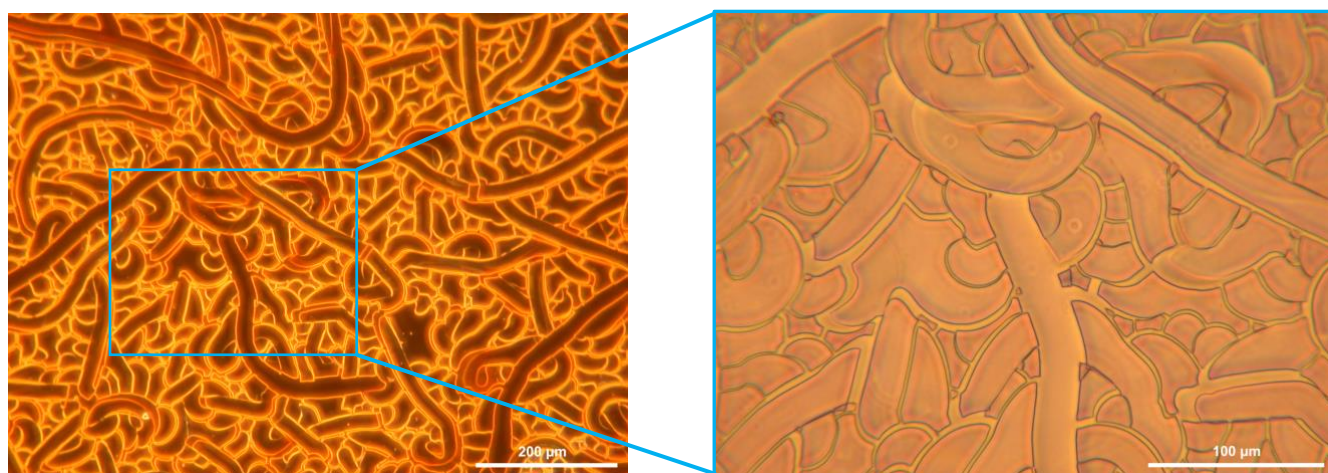
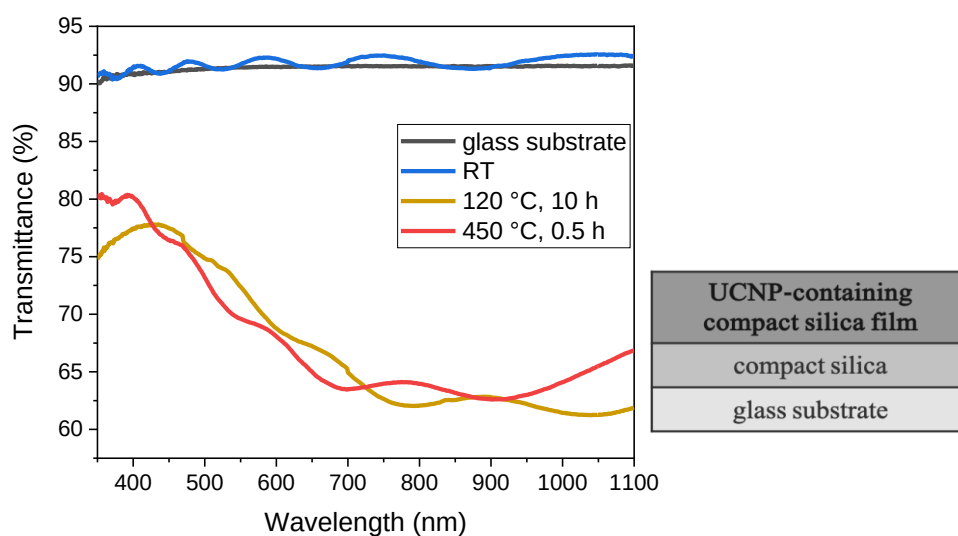


Figure 17. Transmission spectra of composite thin films of UCNP's with different matrices: silica matrix (top) and microscopic image of the cracked surface of the silica matrix composite thin films of NaYF₄: 20% Yb, 0.5% Tm UCNP's (bottom)

The light scattering did not only occur in the lower wavelength region, meaning that the inhomogeneities in the heat-treated samples were greater in size (not nano-scaled imperfections). I also examined the thin films under optical microscopy and observed a characteristic crack pattern (Figure 17 bottom). The curved geometry of the crack tips indicates that complex physical-chemical processes cause the coatings to fracture during heat treatment. The presence of nanoparticles could be the reason for the cracked coating during annealing. A possible explanation for this is that there is a strong difference between the thermal expansions of the matrix ($\alpha(\text{SiO}_2) = 0.55 \cdot 10^{-6} \text{ K}^{-1}$)⁵⁴ and that of NaYF_4 ($\alpha(\text{UCNP}) = 27.2 \cdot 10^{-6} \text{ K}^{-1}$)⁵⁵. This phenomenon only occurred in case of silica matrix thin films. The thermal expansion of titania ($\alpha_{\text{surface}}(\text{TiO}_2) = 10,4 \cdot 10^{-6} \text{ K}^{-1}$)⁵⁶ is closer to that of UCNPs.

Figure 18 shows the transmission spectra of differently heat-treated or dried (at room temperature) titania matrix composite thin film. After the annealing step, the number of minimums and maximums decreased in the spectra, meaning that the layer thickness of the coatings decreased after heat treatment.

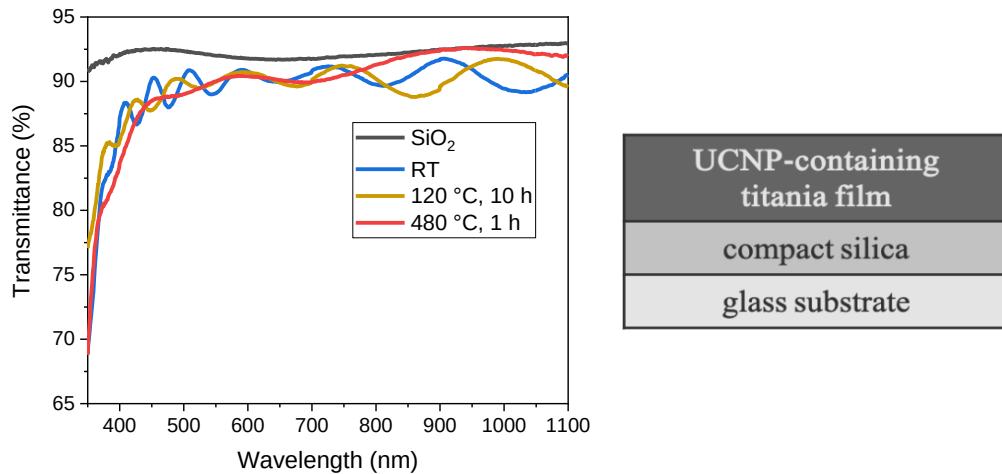


Figure 18. Transmission spectra of composite thin films of UCNPs with titania matrix material

The results of ellipsometric porosimetry measurements of chitosan and chitosan/UCNP coatings on Si substrates were the following: the thickness of the UCNP-free chitosan coating was 95 nm, while the chitosan matrix composite coatings of UCNPs were 109 nm. Increasing relative pressure, the thickness of the coatings increased to 131 nm and 135 nm respectively due to an uptake of adsorptive material (water). The results indicate that the size of UCNPs (about $\varnothing 40$ nm) can be compared to the size of a layer of coating itself (109 nm). The graphs obtained through the EP measurement can be seen in Figures 19. and 20.

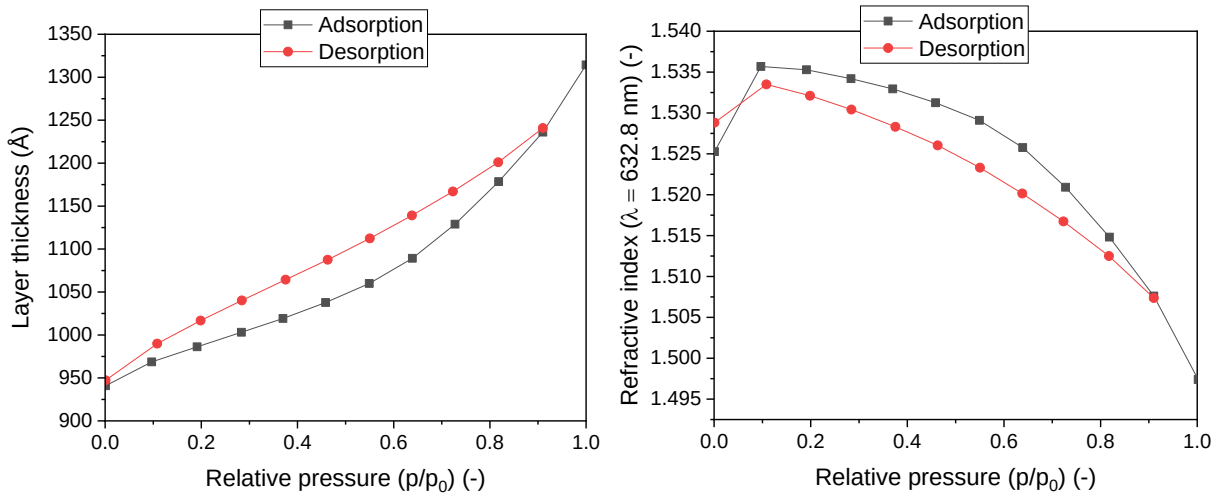


Figure 19. Result of the EP measurement for the chitosan coating on Si substrate (no UCNPs)

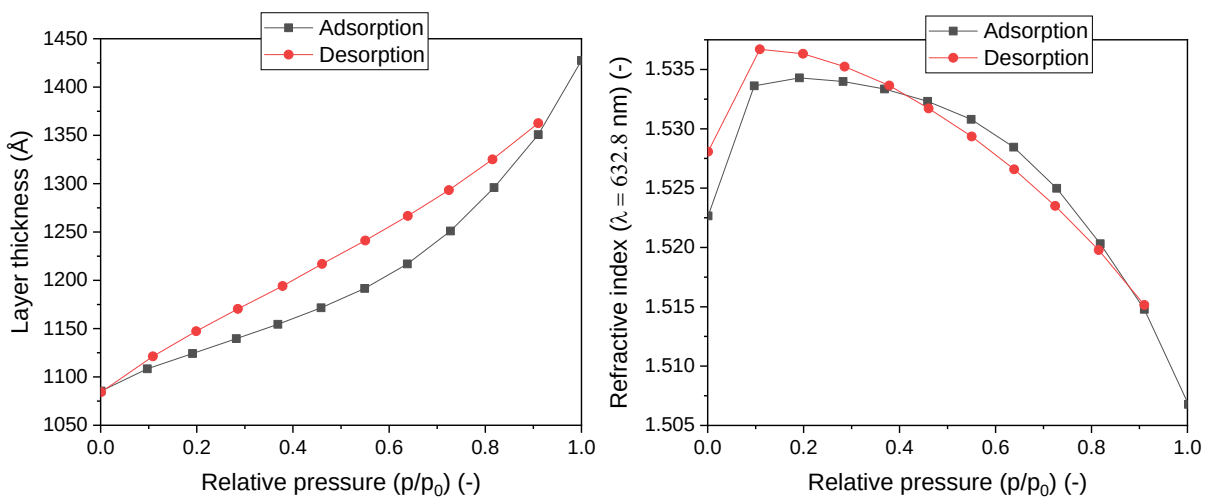


Figure 20. Result of the EP measurement for the chitosan matrix coating of UCNPs on Si substrate (one layer, prepared from 10 mg/mL NaYF₄: Yb, Tm UCNP-chitosan suspension)

5.4 Emission properties of composite coatings

Non-composite coatings of NaYF₄: Yb, Tm UCNPs:

First, the emission intensities of coatings made from ethanolic UCNP suspensions are compared to chitosan matrix composite films of UCNPs (Figure 21). It can be seen that the use of composite coatings is necessary to achieve greater emission intensities.

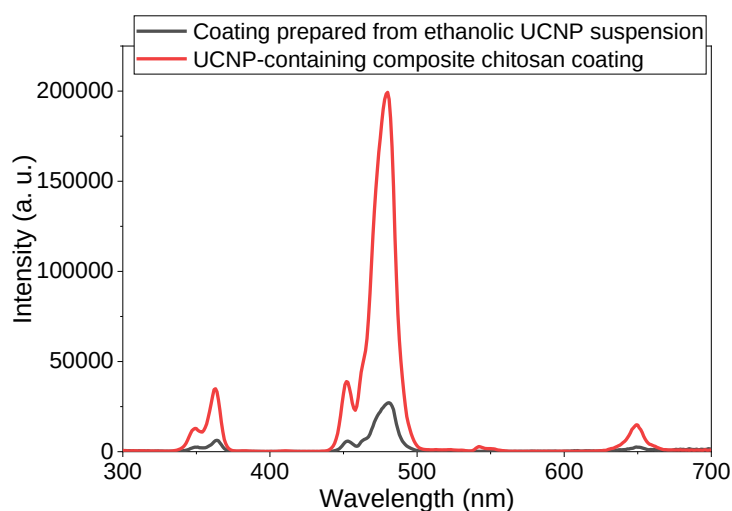


Figure 21. Emission spectra of coatings prepared from 10 mg/mL ethanolic UCNP suspensions and UCNP-chitosan suspensions (NaYF₄: 20% Yb, 0.5% Tm)

Silica matrix composite coatings of NaYF₄: Yb, Tm UCNPs:

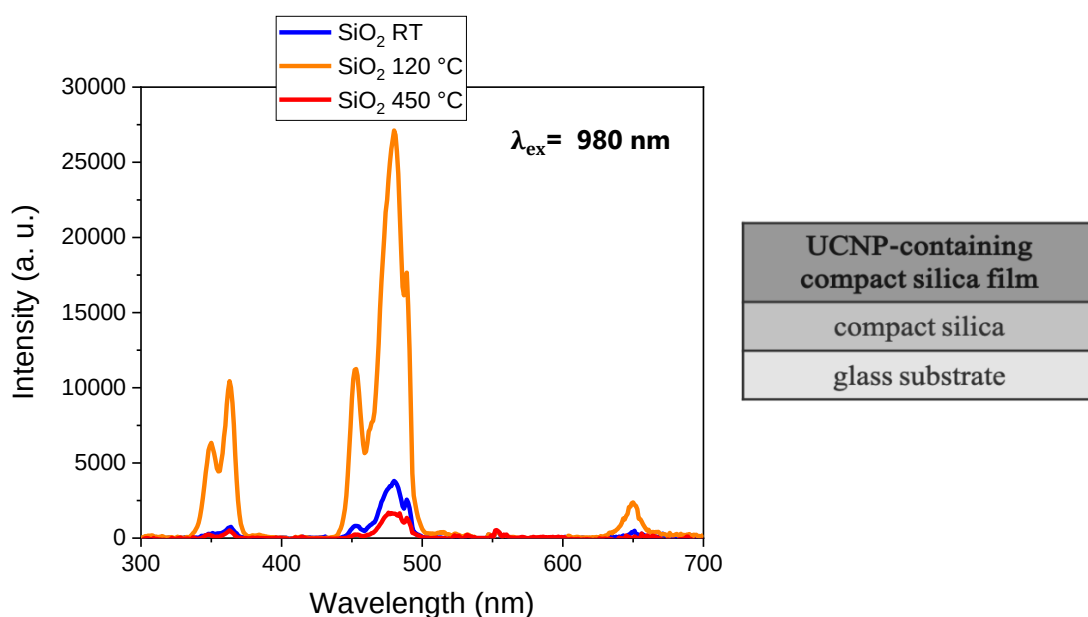


Figure 22. Emission spectra of composite coatings prepared from 10 mg/mL UCNP-containing silica precursor sol (NaYF₄: 20% Yb, 0.5% Tm): effect of annealing on the upconversion emission intensity

The emission spectra of silica matrix thin films of UCNPs can be seen in Figure 22. For the coatings annealed at 120 °C for 10 hours, the heat treatment had a beneficial effect on the upconversion emission intensity. The intensities were increased compared to the untreated coatings. It was found that after heat treatment at 450 °C the emission intensity greatly decreased. However, heat treatment is necessary to improve the mechanical properties of the thin film, without it the properties can be easily damaged, the properties can change over time as the coating changes in air without control, without proper heat treatment the silica matrix still contains ethanol, remaining reagents and impurities.

It is also likely that the afore-mentioned cracked structure influenced the location of microphases on the surface. These results suggest that compact silica is a suitable matrix material for lanthanide-doped NaYF₄ upconverting nanoparticles, but it would be advisable to avoid crack formation by using a different type of colloidal particle or a different annealing step. This could also be achieved by modifying the composition of the silica matrix (via surface modification for example). Further research is required to achieve the optimal coating process for silica matrix thin film systems.

Titania matrix composite coatings of NaYF₄: Yb, Tm UCNPs:

In case of titania matrix material (created for photoactivity-related applications) annealing at 120 °C decreased the emission intensities of the coatings and annealing at 480 °C resulted in a complete loss of upconversion photon emission. The results for NaYF₄: Yb, Tm are presented in Figure 23. Titanium dioxide is already partially crystalline when heated at higher temperatures this is beneficial for mechanical properties but the upconverting nanoparticles lose their upconversion emission properties at this temperature, presumably due to the decomposition of organic ligands. Crystalline anatase phase is formed in the titanium dioxide layer at 480 °C, which can affect the upconversion emission properties of the composite system, and previous measurements of powder samples have shown that annealing at this temperature leads to a significant decrease in the upconversion particle emission.

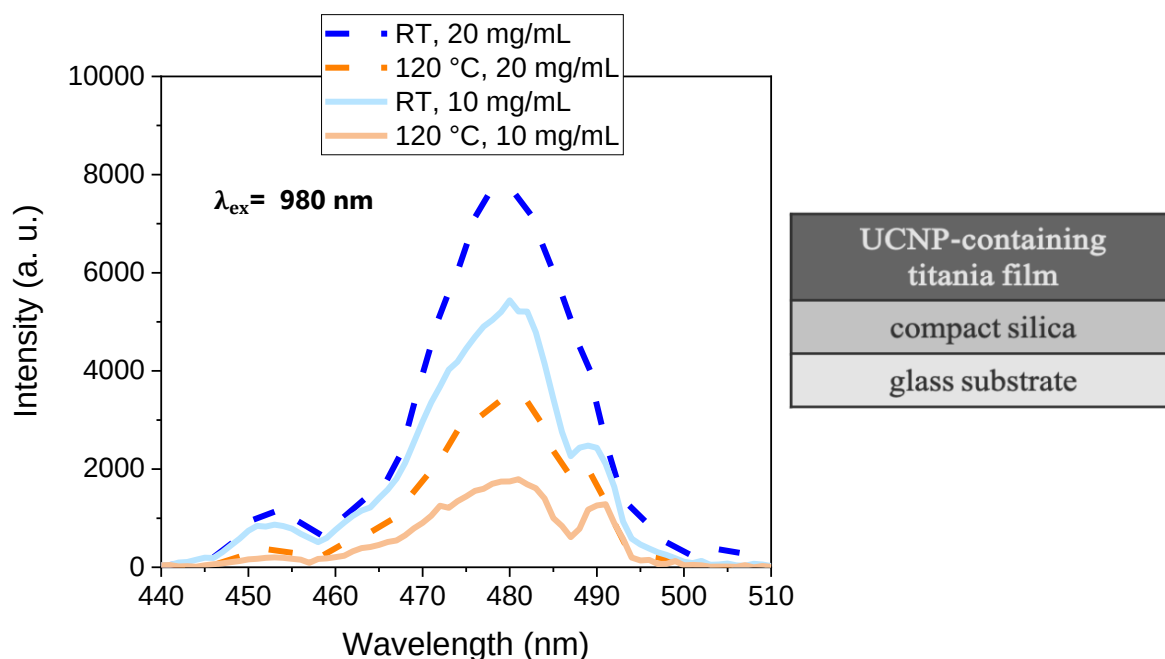


Figure 23. Emission spectra of composite coatings prepared from 10 or 20 mg/mL UCNP-containing titania precursor sol (NaYF₄: 20% Yb, 0.5% Tm): effect of annealing on the upconversion emission intensity (heat treatment at 480 °C reduces the emission intensity to zero)

Titania matrix composite coatings of LaF₃: Yb, Tm UCNPs:

To counter this decrease and complete loss of emission intensity LaF₃: Yb, Tm samples were tested in titania matrix composite thin films. Previous research of the research group showed that annealing at higher temperatures (300...600 °C) results in an increase of upconversion emission intensity in case of LaF₃ lattice UCNPs.²⁶ The emission spectra of untreated and annealed (at 480 °C) titania matrix composite thin films of LaF₃: Yb, Tm UCNPs can be seen in Figure 24.

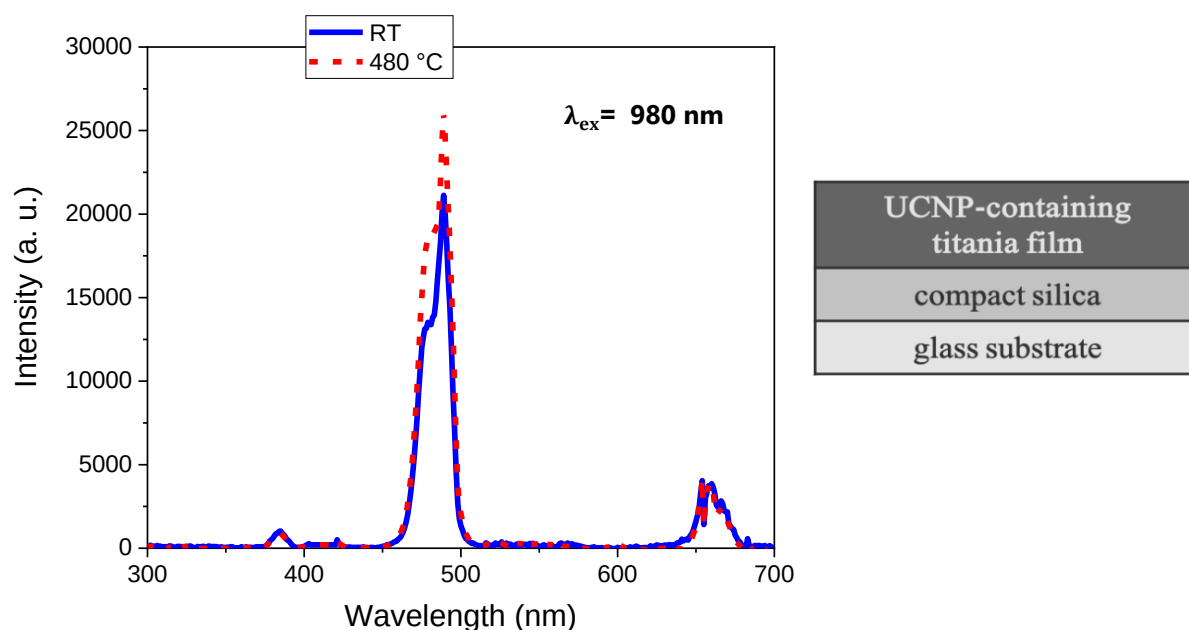


Figure 24. Emission spectra of composite coatings prepared from 10 mg/mL UCNP-containing titania precursor sol (LaF_3 : 4% Yb, 0.1% Tm): effect of annealing on the upconversion emission intensity

The results in titania matrix composite coatings of LaF_3 -based UCNPs coincide with the results in suspensions: annealing slightly increased the emission properties of these composite coatings. Using LaF_3 as a host lattice for upconverting nanoparticles allows them to be utilised in titania matrix thin films. The emission intensities are retained after proper heat treatment: Annealing is mutually beneficial for both UCNPs and the titania matrix material of the composite coatings. Physical-chemical properties of LaF_3 -based UCNPs and titania precursor sol made it possible to create such concentrated coatings.

Chitosan biopolymer matrix composite coatings of NaYF₄: Yb, Tm UCNPs:

Lastly, I will analyse the results of the experiments with chitosan biopolymer matrix composite thin films of NaYF₄: Yb, Tm upconverting nanoparticles. No heat treatment is required (nor would it be possible) when using chitosan as matrix material, drying the coatings at room temperature is sufficient to achieve the final, stable structure of these films. Figure 25 shows the emission spectra of composite coatings prepared using silica and chitosan matrix material: The emission intensity of the composite chitosan coatings is significantly higher than that of compact silica coatings with the same number of layers and UCNP-content annealed at 120 °C. Moreover, as shown by the subsequent experimental results, chitosan matrix thin films retain their high emission intensity when immersed in a dye solution for long periods of time, and energy transfer interaction between the dye and the UCNP fixed in the coating can be observed using chitosan matrix composite coatings (see Figure 33).

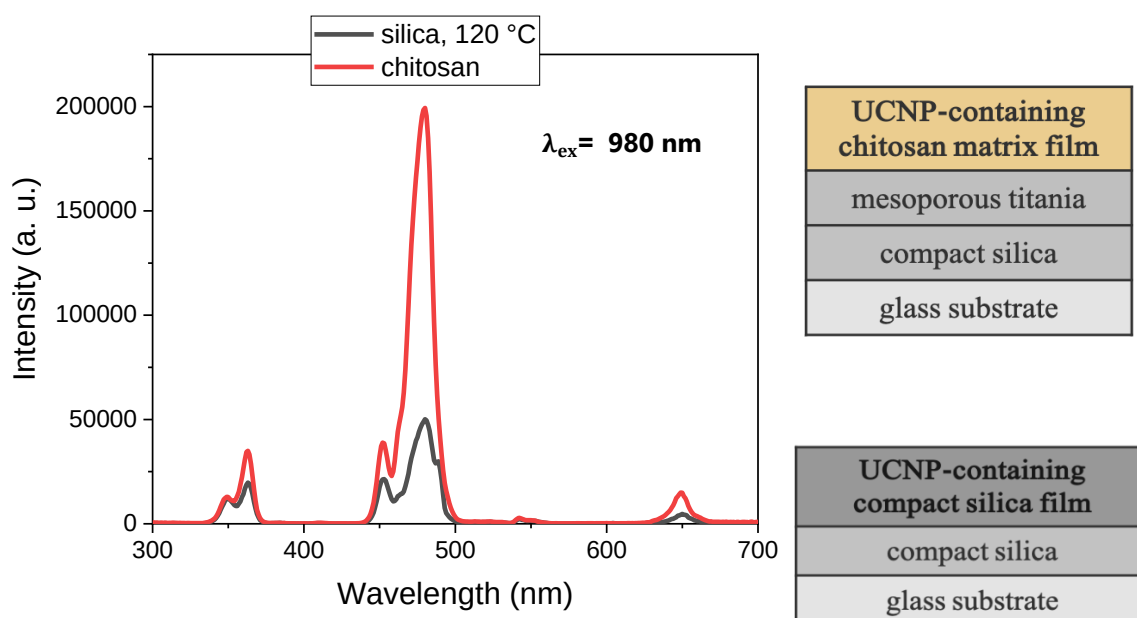


Figure 25. Comparison of the emission spectra of composite coatings prepared from 10 mg/mL NaYF₄: 20% Yb, 0.5% Tm UCNP-containing chitosan suspension or silica precursor sol (3 consecutive layers of composite coatings)

Chitosan matrix material proved to be the best candidate for a multi-purposed functional coating of UCNPs. Because of that I thoroughly studied the effect of layer thickness of the chitosan matrix thin films (Figure 26 left). As the layer thickness increases, the emission intensity also increases, so I designed coatings with 3 layers for further measurements. In addition, the emission intensity of samples with coatings on both sides is higher (Figure 26 right).

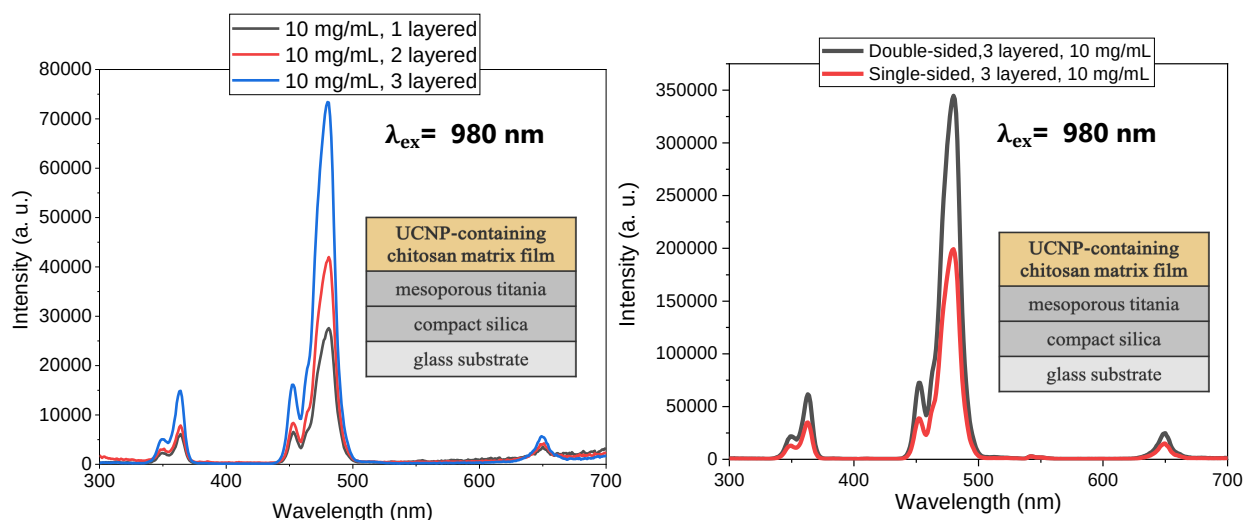


Figure 26. Emission spectra of chitosan matrix composite coatings of UCNPs (NaYF₄: 20% Yb, 0.5% Tm): comparison of 1,2 or 3 layered coatings (left) and thin films prepared from 5 or 10 mg/mL UCNP-containing chitosan precursor (right)

The emission spectra of three-layered chitosan coatings formed from 5 or 10 mg/mL upconverting nanoparticle suspensions are shown in Figure 27. It is observed that the emission intensity increases with increasing concentration of the precursor suspension. Experiments have also been carried out with coatings formed from suspensions with a UCNP content of 20 mg/mL, but more concentrated suspensions are difficult to work with, as it is impossible to create a kinetically stable dispersion using such a large amount of upconverting colloidal particles and viscous chitosan solution, making it unsuitable for coating formation.

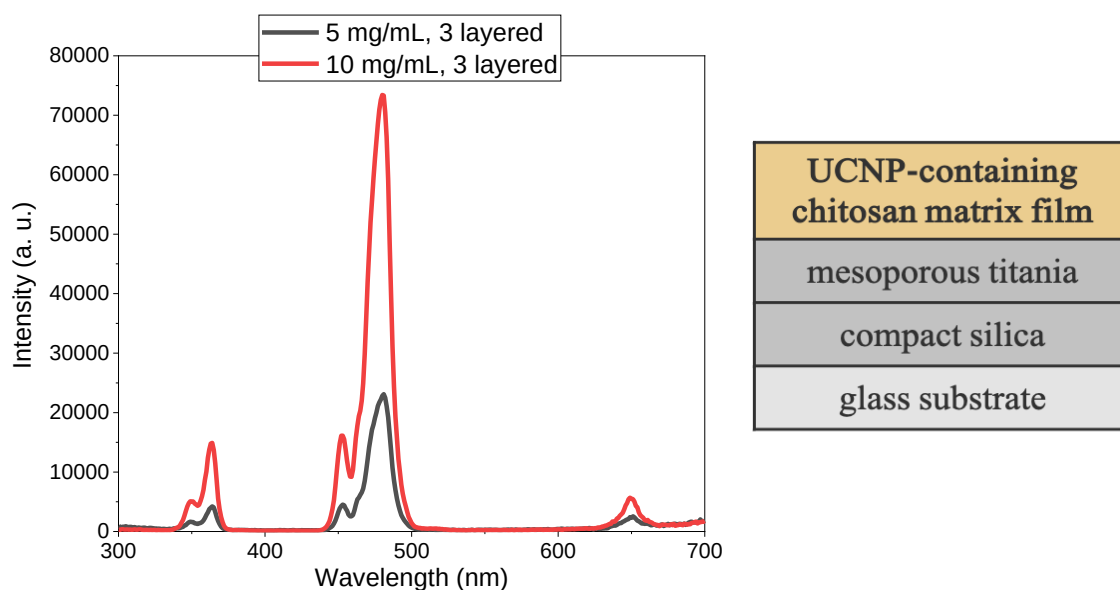


Figure 27. Emission spectra of chitosan matrix composite coatings of UCNPs (NaYF₄: 20% Yb, 0.5% Tm): comparison of thin films prepared from 5 or 10 mg/mL UCNP-containing chitosan precursor

5.5 Characterisation of energy transfer processes between UCNPs and Rhodamine 6G

The energy transfer interactions of upconverting nanoparticles are of utmost importance in many possible applications (i.e. drug-release systems, photovoltaic devices, dye-sensitised sensors). Such energy transfer interactions of NaYF₄: Yb, Tm UCNPs were investigated using Rhodamine 6G fluorescent dye as a model material. The possibility of energy transfer between these two components can be understood from Figure 28: The emission of the UCNP suspension in the 440...500 nm wavelength range partially overlaps with the absorption peak of Rhodamine 6G.

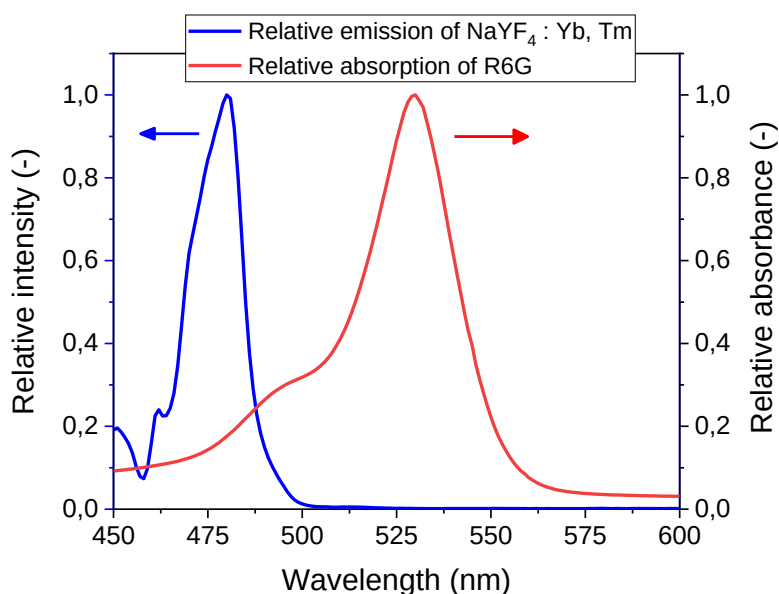


Figure 28. Emission spectra of chitosan matrix composite coatings of UCNPs (NaYF₄: 20% Yb, 0.5% Tm): comparison of 1–3 layered coatings (left) and thin films prepared from 5 or 10 mg/mL UCNP-containing chitosan precursor (right)

Energy transfer processes in case of UCNP suspensions:

The 1 mg/mL UCNP suspension (without dye solution) emits photons both in the visible and UV region of electromagnetic radiation upon excitation at 980 nm wavelength, but no emission peak can be detected at 554 nm wavelength, typical for the Rhodamine 6G dye molecule. When the R6G dye solution is subjected to 980 nm excitation, no emission peaks are observed at all, since the absorption peak of Rhodamine 6G dye solution is located at 530 nm wavelength, it cannot be excited at 980 nm wavelength. However, if R6G dye is added to UCNP suspensions the intensity of the emission peak (at 480 nm wavelength) that potentially excites Rhodamine 6G decreases in intensity and a new emission peak (at 555 nm wavelength) characteristic of Rhodamine 6G appeared (Figure 29). A scheme explaining the interaction between the two components can be seen in Figure 30.

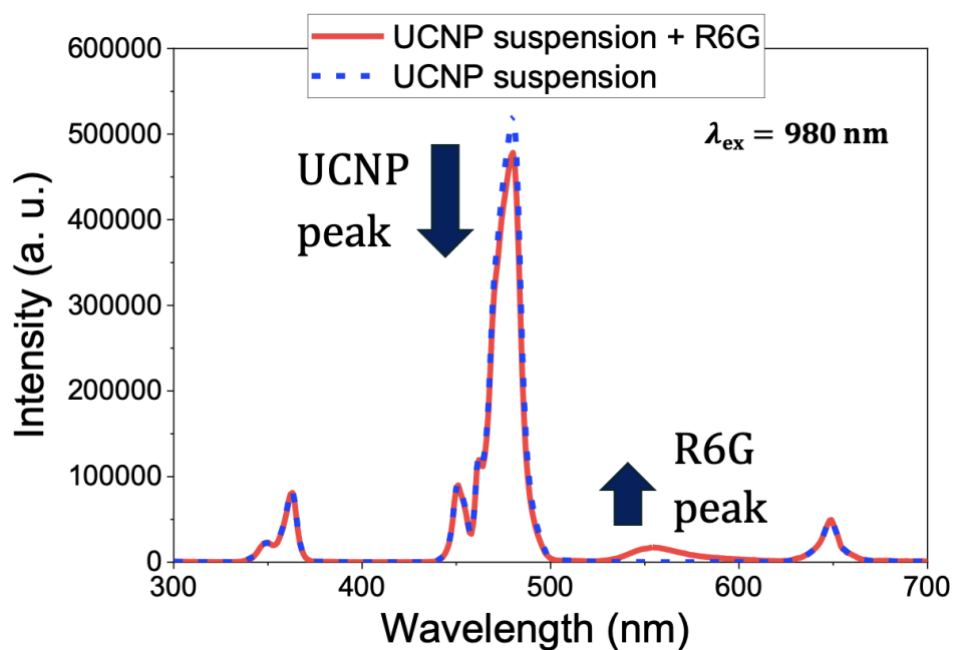


Figure 29. Emission spectra of 1 mg/mL ethanolic UCNP suspension (NaYF₄: 20% Yb, 0.5% Tm) without R6G dye molecules (blue spectrum) and with 5 μM R6G dye concentration (red spectrum).

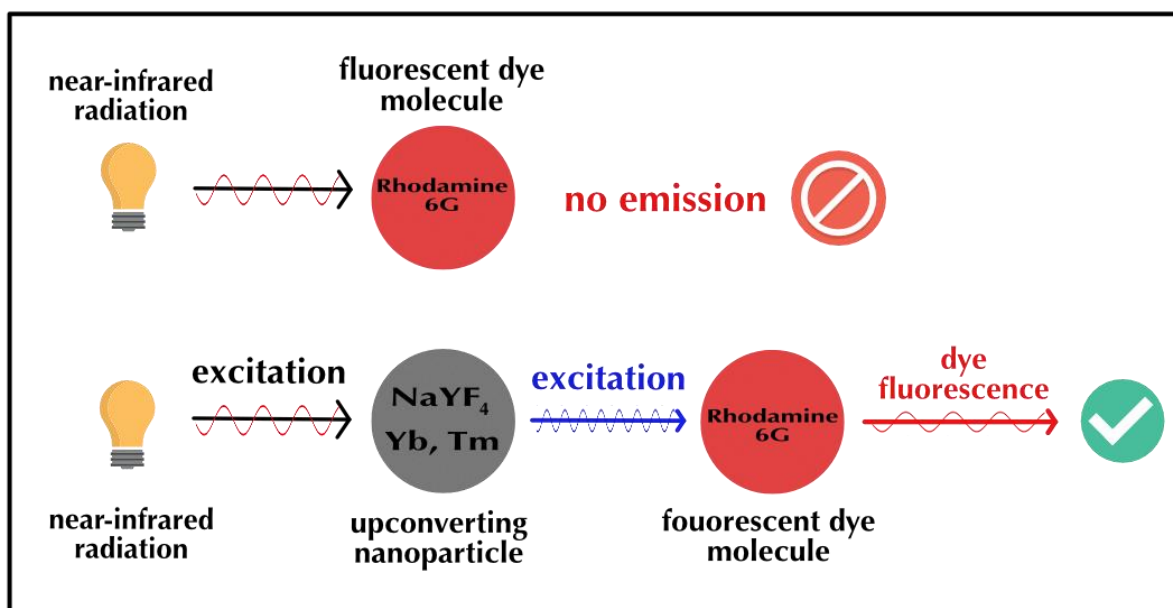


Figure 30. A schematic overview of the energy transfer interaction between NaYF₄: 20% Yb, 0.5% Tm UCNPs and Rhodamine 6G dye molecules under 980 nm NIR irradiation

Figure 29 shows the emission spectra of suspensions of 1 mg/mL NaYF₄: Yb, Tm and 1-20 μ M Rodamine 6G. It was observed that with increasing dye concentration, the intensity of the 480 nm emission peak continually decreased, and the 554 nm emission peak increased in intensity (Figures 31 and 32). Based on my literature research, it can be stated that Förster resonant energy transfer (FRET) takes place between the dye molecules and the upconverting nanoparticles.^{17,57} The explanation for the appearance of a new emission peak characteristic of the R6G dye is that the upconverting nanoparticles can excite the dye molecules, which upon relaxation exhibit photon fluorescence.

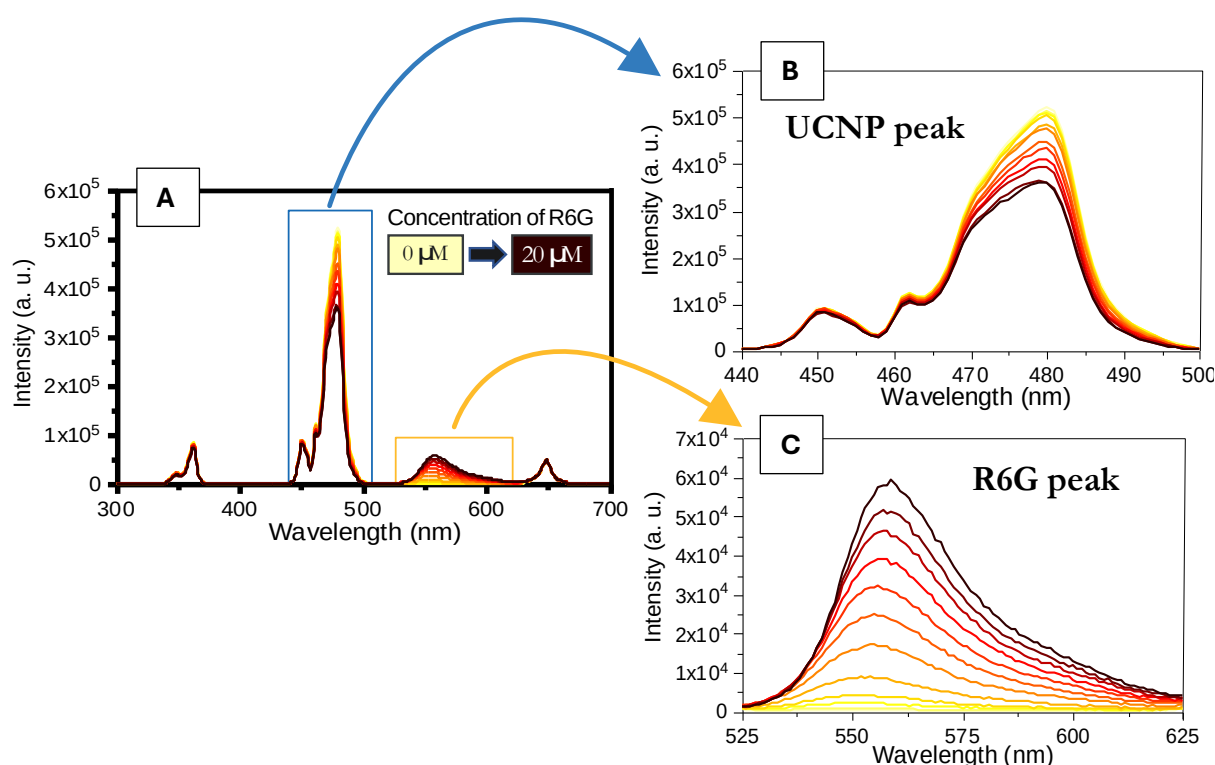


Figure 31. Emission spectra of 1 mg/mL ethanolic UCNPs suspensions (NaYF₄: 20% Yb, 0.5% Tm) with a R6G dye concentration of 0...20 μ M (A). The 480 nm wavelength UCNP emission peak and the R6G fluorescence peak at 554 nm wavelength enlarged (B and C).

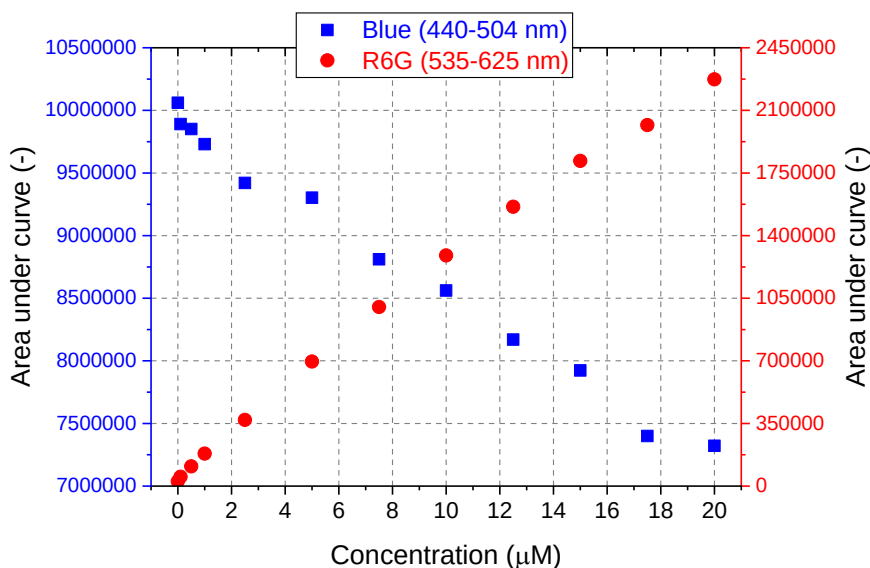


Figure 32. Area under a specific region of the emission spectra of 1 mg/mL ethanolic UCNP suspensions (NaYF₄: 20% Yb, 0.5% Tm) containing 0...20 μM R6G

Energy transfer processes in case of composite coatings: Chitosan matrix composite coatings of upconverting nanoparticles immersed in R6G dye solution produced similar results as UCNP suspensions: an emission peak characteristic to the Rhodamine 6G dye was detected under NIR excitation. The phenomenon was investigated in ethanolic dye solution. By placing the coatings in an ethanol medium, a constant emission intensity can be achieved over a long period of time, It can be observed that the intensity ratio of the UCNP emission peak at 480 nm wavelength of dye excitation and the fluorescence emission peak of the dye (554 nm) are almost the same as for the chitosan matrix coating immersed in an ethanolic dye solution and an ethanolic UCNP suspension containing dye molecules (Figure 33). Thus, it can be stated that the chitosan matrix material does not hinder the energy transfer process between UCNPs and dye molecules. Very similar results can be obtained when the UCNPs are bound in the chitosan matrix as to when the microphases and dye molecules are both mobile in a suspension. The mechanism of the energy transfer process in case of composite coatings could be Förster resonant energy transfer (as reported previously in case of suspensions¹⁷). However FRET requires small distances between the donor and acceptor, so it would require the dye molecules to migrate into the coating. Another possible mechanism could be that the upconversion photon emission of the composite coating excites the dye molecules in the solution in which the coating is immersed. Further studies are required to determine the exact mechanism of the energy transfer process between dye molecules and UCNPs embedded in composite coatings.

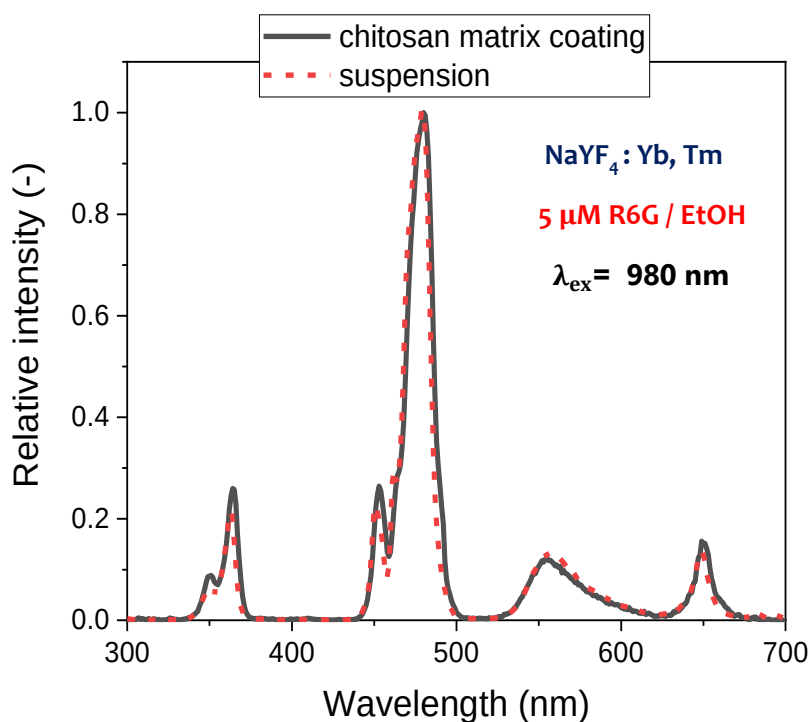


Figure 33. Comparison of emission spectra of 1 mg/mL ethanolic UCNP suspension with 5 μ M R6G dye concentration (red spectrum) and chitosan matrix composite coating (10 mg/mL) of UCNPs immersed in 5 μ M R6G dye solution.

The concentration dependence of the energy transfer process was also investigated in case of chitosan matrix thin film systems. The results can be seen in Figures 34 and 35. In case of composite coatings higher dye concentration was required to achieve the same results as in dye-containing UCNP suspensions. The intensity of the dye emission peak showed a maximum in case of coatings, where the UCNP photon emission peak showed an ever-decreasing trend. A possible explanation for this maximum could be the self-quenching of the dye molecules at high concentrations⁵⁸.

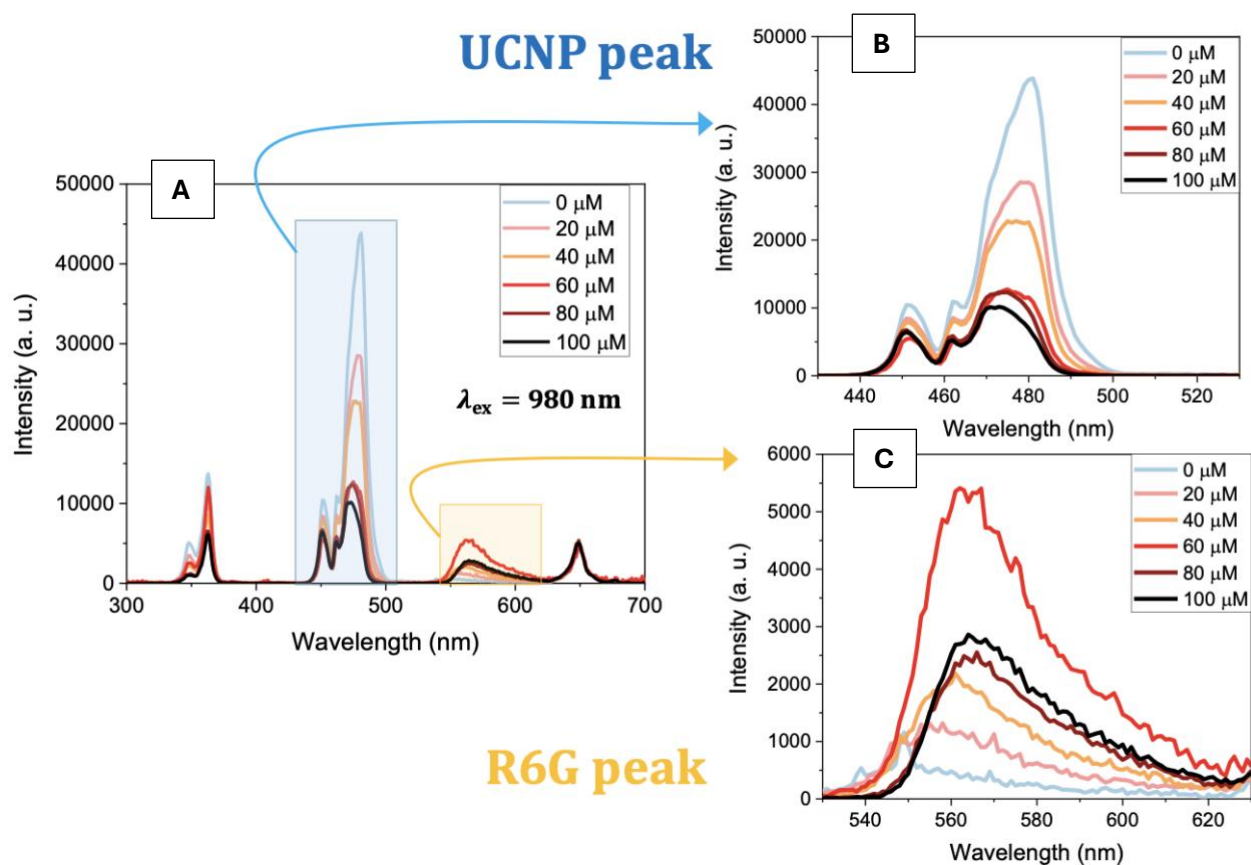


Figure 34. Emission spectra of chitosan matrix composite coating (prepared from a 10 mg/mL UCNP-chitosan suspension) with a R6G dye concentration of 0...100 μM . The 480 nm wavelength UCNP emission peak and the R6G fluorescence peak at 554 nm wavelength can be seen enlarged on the right side of the figure.

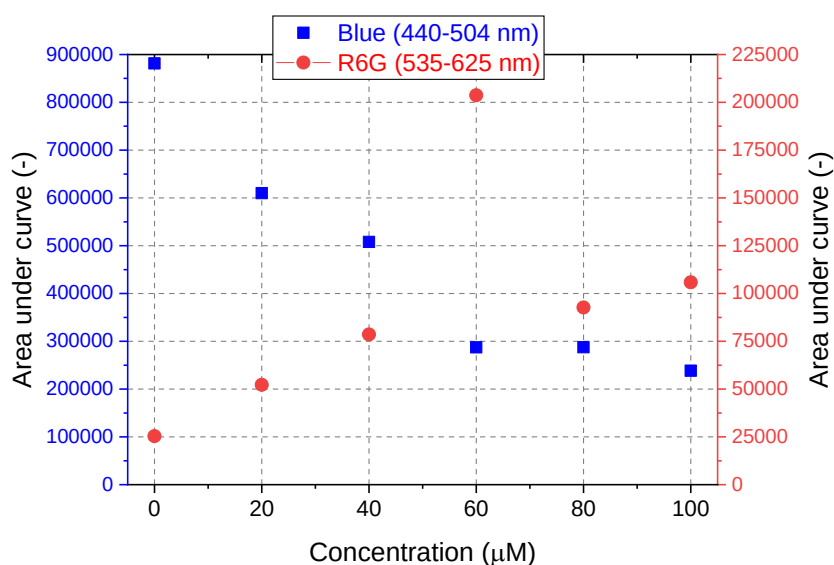


Figure 35. Area under a specific region of the emission spectra of chitosan matrix composite coatings of UCNPs immersed in a R6G dye solution of 0...100 μM concentration

6 Conclusions

In our research work, NaYF₄: 20 % Yb³⁺, 0.5 % Tm³⁺ upconverting nanoparticles were synthesized via solvothermal method. The nanoparticles showed high upconversion emission intensities under 980 nm excitation. Composite coatings of UCNPs were prepared via spin-coating process, in which silica, titania, and chitosan were used as matrix material. The preparation parameters were optimised in terms of maximising the achieved emission intensity: the type of matrix material, heat treatment, film thickness, and UCNP content were considered. The highest emission intensities were achieved using chitosan biopolymer as matrix material. The coating preparation parameters that resulted in the highest achieved upconversion emission intensities are summarised in Table 6.

Table 6. Summary of the composite coatings with most promising emission properties

Type of coating	Optimal heat treatment	Type of UCNPs	Conclusions
SiO ₂ /UCNP	120 °C, 10 h	NaYF ₄ : Yb, Tm	Cracked surface, high emission intensity
TiO ₂ /UCNP	480 °C, 1 h	LaF ₃ : Yb, Tm	Acceptable upconversion emission intensity after high temperature annealing
chitosan/UCNP	No heat treatment	NaYF ₄ : Yb, Tm	Highest emission intensity, accessible to smaller molecules (i. e. dyes)

Selected photos and videos about the upconversion phenomenon can be seen in Figure 36 (photos and videos were created by me). These visual examples illustrate well that upconverting nanoparticles emit light in the visible region under NIR irradiation. This can be observed with the naked eye both in powder form and in chitosan matrix composite films.

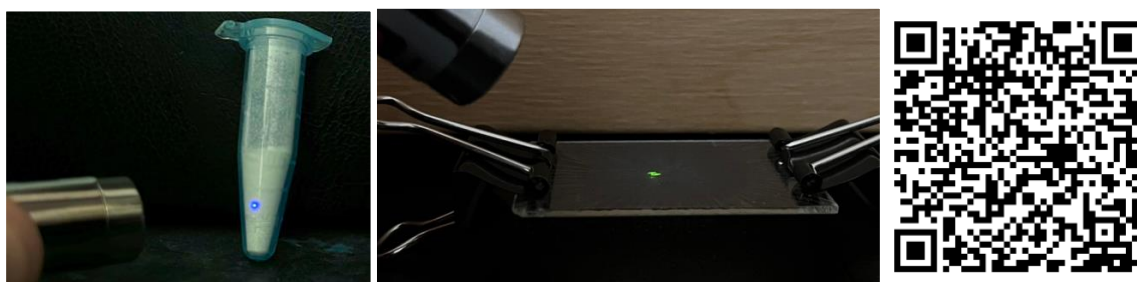


Figure 36. Samples irradiated by 980 nm NIR laser light source: Tm-doped UCNPs-powder (left), chitosan matrix composite coating of Er-doped UCNPs (middle) and a [QR-code](#) (right) leading to videos demonstrating the upconversion phenomenon (see Appendix for details on the Er-doped UCNPs)

Energy transfer processes between UCNPs and Rhodamine 6G (R6G) model fluorescent dye molecules were also studied in a system containing both fluorescent dye molecules and UCNPs (UCNP suspensions of aqueous dye solutions; or chitosan-matrix thin films immersed in aqueous dye solutions). Under 980 nm NIR-excitation, the fluorescent emission peak of R6G appeared in the emission spectrum even though the absorbance of the dye is in the visible region. Hence, it was proved by the experiments that the upconverting nanoparticles were capable of exciting the dye molecules under NIR irradiation, even in the case of the composite coating systems.

My yet unpublished, new results in the composite, nanostructured coatings of UCNPs show great potential in this area of scientific innovation, we aim to publish our results in a scientific journal shortly.

Our future aims include a deeper analysis of the effect of the composition of the matrix materials, and the detailed study of the energy transfer processes in composite coatings. This would also help with the development of an efficient sensor based on UCNPs embedded in a matrix material with optimal structure and composition.

As it was mentioned before, few publications deal with the investigation of upconversion phenomena in composite coatings. We hope to have contributed to the expansion of scientific literature in the field of upconverting nanomaterials with this paper and our future articles on this topic. We are determined to help bring about sensing, photovoltaic and photocatalytic applications of composite coatings of UCNPs.

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9 Appendix

9.1 Method of thin film optical fitting

Some of the composite coatings were deposited on substrates that contained previously prepared compact silica or titanium dioxide coatings. To characterize these substrates, I performed thin-film optical model fitting on compact silica and porous titanium dioxide coatings created by E. Hild.^{51,52} A description of this is included in the Appendix.

First, I corrected the transmittance of the silica or titania layer using the transmission spectra, refractive index, and dispersion of the glass. The transmittance spectrum of the glass was taken immediately after the cleaning step, the other two quantities are explained in the next paragraph. The correction is necessary because of the low light absorption of the glass substrate. In the thin film optical model fitting, I fitted a non-linear curve to this corrected transmittance spectrum.

The refractive index, dispersion factor and lamp intensity of the glass substrate were set to constant values. The refractive index value for both the glass substrate and the coating is associated with a wavelength of 632.8 nm. The dispersion factor is a quantity expressing the frequency dependence of the refractive index for both the glass plate and the coatings, and the lamp intensity value of 1 expresses the time constant of the intensity of the excitation light source. The accuracy of the fit was further improved by varying the dispersion factor (q) and the inhomogeneity coefficient (g) of the coating. The curve fitting resulted in approximate values for the coating thickness (one-hundredth of its value in nm units) and refractive index (at a wavelength of 632.8 nm).

In evaluating the fitted curve, I made sure that the physical content of the fitted function data was as close to reality as possible, and that the value of reduced χ^2 was in the magnitude of $10^{-9} \dots 10^{-7}$.

The fitting parameters of the model applicable to compact silica coatings are summarized in Table 7.

Table 7. Thin film optical fitting parameters for silica coatings on glass substrates

	Parameter	Initial value	Fixed?
n_0	refractive index of coating [-]	1.45	no
d	layer thickness [nm/100]	2	no
g	optical inhomogeneity of layer [.]	1	no
q	dispersion factor [-]	0	no
p_1	refractive index of glass substrate [-]	1.52	yes
p_2	dispersion factor of glass substrate	0.3	yes
k_k	lamp intensity	1	yes

For porous TiO₂ thin films, the compact silica layer underneath the coating had to be considered. In Table 8, index 1 indicates the physical properties of the porous titania coating and index 2 indicates the silica coating underneath.

Table 8. Thin film optical fitting parameters for titanoa coatings on SiO₂/glass substrates

	Parameter	Initial value	Fixed?
n_1	refractive index of porous TiO ₂ layer	1.62	no
n_2	refractive index of compact SiO ₂ layer	1.45	no
d_1	layer thickness of porous TiO ₂ layer	1	no
d_2	layer thickness of compact SiO ₂ layer	2	no
p_1	refractive index of glass substrate [-]	1.52	yes
p_2	dispersion factor of glass substrate	0.3	yes
q_1	dispersion factor of porous TiO ₂ layer	3	no
q_2	dispersion factor of compact SiO ₂ layer	0.3	no
k_k	lamp intensity	1	yes

According to the Lorentz-Lorenz equation, the effective refractive index obtained as a result of the fitting can be used to calculate the porosity of thin films:

$$\frac{n_{\text{eff}}^2 - 1}{n_{\text{eff}}^2 + 2} = \alpha \cdot \frac{n_b^2 - 1}{n_b^2 + 2} + (1 - \alpha) \cdot \frac{n_{\text{air}}^2 - 1}{n_{\text{air}}^2 + 2}$$

where:

- n_{eff} is the effective refractive index of the coating (-)
- n_b is the refractive index of the bulk material (-)
- n_{air} is the refractive index of air (1,000)
- α is the volume fraction of a specific component (-)

Porosity can be obtained from the results of the fitting using the following formula:

$$P = (1 - \alpha) \cdot 100\%$$

The model on which the fitting is based can no longer be used to characterise the physical properties of coatings with 3 or more layers, so I could not characterise my glass substrates with chitosan layers. The intense light scattering of the upconverting nanoparticles in their composite coatings is also a boundary for this model. Ellipsometric porosimetry measurements can take into account the effect the microphases have on the optical properties of the composite coatings (See 4.3.5 and 5.3)

9.2 Characterisation of NaYF₄: Yb, Er UCNPs (demonstrative purposes)

Chitosan matrix composite thin films of commercially available NaYF₄: Yb, Er (NaY_{0.77}Yb_{0.20}Er_{0.03}F₄, Sigma Aldrich, 99%) were also prepared using the same method as stated before.

The emission spectrum of a composite coating prepared from 10 mg/mL NaYF₄: Yb, Er-chitosan suspensions can be seen in Figure 37.

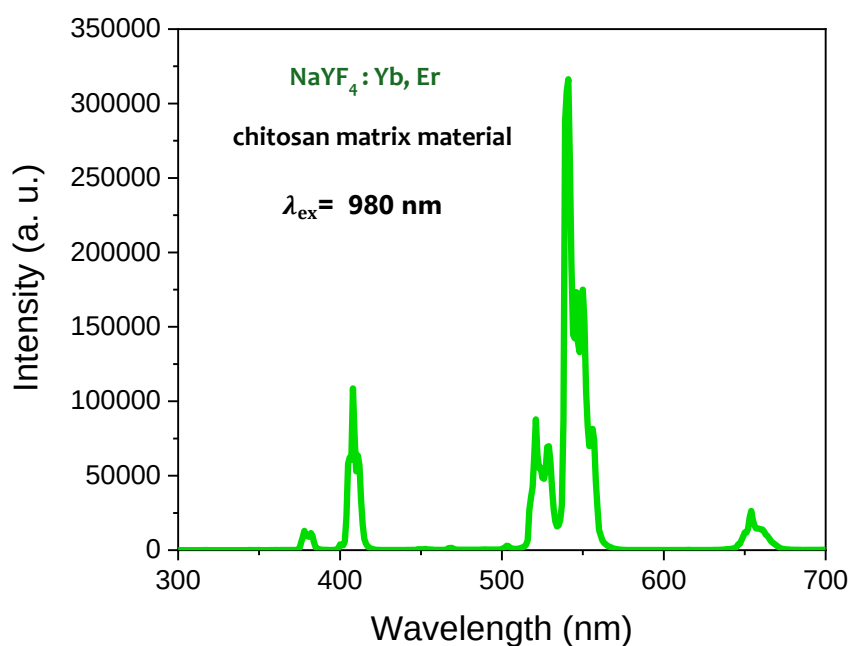


Figure 37. Emission spectrum of a chitosan matrix composite thin film of NaYF₄ : Yb, Er UCNPs (3 layered, prepared from a 10 mg/mL UCNP-chitosan suspension)

These coatings were created for demonstration reasons because the 540 nm wavelength green upconversion photon emissions of these nanoparticles are of high intensity and can easily be detected even by the naked eye or using a camera. These coatings are able to make NIR light visible, which highlights the interesting, unusual field of upconversion photon luminescence and the importance of upconverting nanoparticles in this area (Figure 38).



Figure 38. Samples irradiated by 980 nm NIR laser light source ($P < 50$ mW): Er-doped UCNPs-powder (left) and chitosan matrix composite coating of Er-doped UCNPs (right)