Non Linear Quantum Yield of Upconverting Nanoparticles

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1 Introduction

1.1 Upconverting nanoparticles: $NaYF_4$:RE

Upconversion (UC) consists in a multiple photon absorption followed by single photon emission after an energy transfer process, thereby the emitted photons are more energetic. Despite of this unique property, upconverting nanoparticles (UCNP's) are photostable, present long fluorescent lifetime, and do not have the photoblinking effect as it occurs in quantum dots. Because of these characteristics, they have potential promising applications to improve solar energy systems, and in biological applications as contrast agents. For the latter, one of the biggest challenges is how to improve their UC efficiency.

When codoped with $Yb^{3+}$and Tm^{3+}, the UCNP's are able to absorb near infrared (NIR) ($965\ nm$) , which has deep tissue penetration, and emit higher energy near infrared and visible light (peaks at $474\ nm$, $644\ nm$ and $800\ nm$) in an anti-stokes process. Electrons on the f-shell of Yb^{3+}ions (sensitiser) absorb NIR photons and after an excitation/relaxation process transfer their energy to f-shell electrons of Tm^{3+}ions (emitter). Electrons of the emitter have long enough life time in excited states in order that they absorb more photons and are excited to even higher energy levels. At the end of the cycle, the electrons from the emitter relax to the ground state emitting higher energy single photons.

Once the upconversion radiation depends on Tm^{3+}ions, the emission spectra can be tuned by replacing the emitter by different lanthanide ions, such as Er^{3+}, Lu^{3+}, or Gd^{3+}. Currently, it is well known that the hexagonal phase (β-phase) of this class of materials when codoped with $Yb^{3+}$and Er^{3+} Tm^{3+} or Lu^{3+} ions is the most efficient in terms of upconversion among the materials with this property [1]. Their efficiency can be evaluated by terms of the so called quantum yield (QY), which is defined by the ratio of the number of photons absorbed by the number of emitted photons normalised by their wavelength. Understanding the efficiency of these NP's is critically important to develop biological applications. The UC process is still not well understood and up to current date, there is only one paper on the literature reporting a process to measure the UC QY.

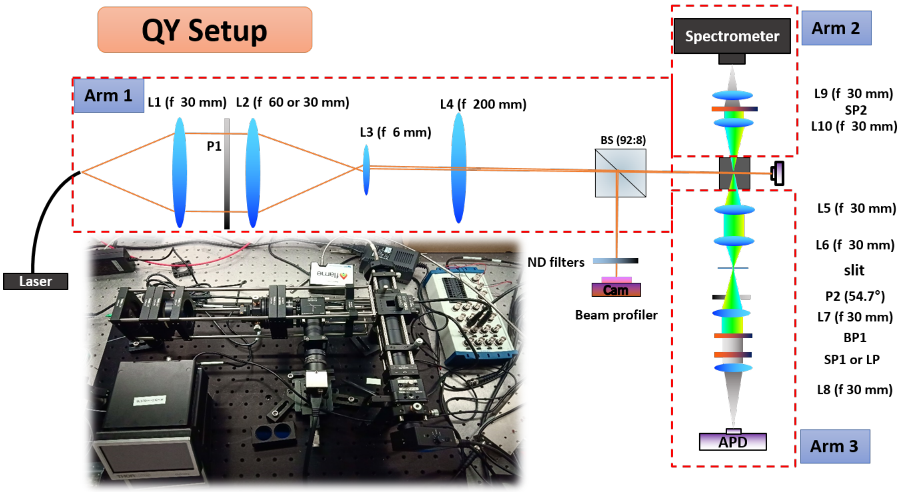
In this work, an experimental setup was built up to measure the emission signal of different UCNP's and a well known dye as a reference. Measuring the light emission of both dye and UCNP, the QY of the latter can be evaluated for different power densities. A non linear quantum yield behaviour lower than 0.5% was observed for power densities bellow $30\ W/cm^2$.

2 Methods

2.1 System setup

The Optical layout of the QY system is shown in Fig. 2. The system was developed based on the previously reported system, which was similar to a conventional fluorometer [2]. The system consists of three arms, i) source arm ii) spectrometer arm iii) QY emission arm. The source arm consists of a single mode fiber laser ($976\ nm$, continuous wave $500\ mW$) which was polarized using a thin film polarizer, and pair of lenses (L1

L2) was used to expand the beam spot size (1 cm) to avoid damage of polarizer. A gaussian beam (FWHM $500\ \mu m$) was produced at the middle of the sample cuvett by arranging two convex lenses (L3 $= 6\ mm$ and L4 $= 200\ mm$). The beam profile was evaluated using a bream profiler (part no.), a beam splitter (92:8) and neutral density filters were used for this purpose. The attenuated laser power after the sample was measured by a commercial powermetre placed right after the cuvette holder. Arm 2 consists of spectrometre which was arranged at 90 degrees on the left hand side of the excitation path in order to measure the emission spectra from the samples. Arm 3 is the QY emission arm, which consists of series of Optical elements (L5,L6,L7,L8) and filters (BP1 or SP1,LP1) to efficiently collect the stokes and anti-stokes shifted light from fluorescence dye and UCNP, respectively. A combination of short, long and band-pass filtres were placed on the emission paths to ensure that only the selected emission wavelength would reach the detectors.



sign	specification
L1,L2,L3,L4	f = 30, 30 or 60, 6, 200 mm
L5,L6,L7,L8	f=30 mm
L9, L10	f= 30mm
BS	92:8
P1, P2	Thin film polarizer
SP1, SP2	Shortpass filter (900 nm)
BP1	Bandpass filter (800 nm 40 nm)
ND filters	OD [1, 2, 3, 4, 5 , 6]
Slit	900 µm
APD	M00478323 (1mm area)
Fibres (single mode)	6.4 µm (polarisation maintaining)
Spectrometer	Ocean Optics (QE Pro)

Figure 1: Schematic layout of the QY Setup, an image of the compact QY System is shown in the inset

All the data were processed using a DAQ device from National Instruments, connected to a laptop. The APD signal and the laser power were acquired while the laser current was swept from $50\ mA$ to $800\ mA$ using a LabView interface.

2.2 Measurement procedure

The relative quantum yield was evaluated for the water soluble core NaYF4 codoped with $Yb^{3+}$and Tm^{3+}(Hangzhou Fluo NanoTech Co. Ltd. - 102-25-804). As reference, the commercial DY-781 dye was diluted in ethanol. The final concentration was obtained after subsequent dilutions until the final absorption was around 10%. For data acquisition, first, the background signal and laser power were measured keeping empty the cuvette holder. Following it, the same procedure was taken for ethanol, DY-781 dye solution at $785\ nm$ excitation, purified water and aqueous UCNP's at $976\ nm$ excitation. The beam profile was evaluated for different laser powers. The entire measurement protocol was completely automated using a LabView interface and all the raw data were treated and analysed by a MATLAB script.

3 Results and Discussion

The luminescence signal acquired with the avalanche photodiode exhibits a non linear behaviour in response to the absorbed power for the NaYF4 upconverting nanoparticles in contrast to the reference DY-781 dye, which has a well known linear behaviour, see Fig. 2.

The UCNP quantum yield exhibits a non linear behaviour showed by the exponential fit on Fig. 3. The inset represents a picture of the laser beam used to excite the samples. Figure 4 shows the laser beam profile with a Gaussian shape with around $500\ \mu m$.

The QY evaluation was successfully achieved using the DY-781 dye as a reference. The QY value, around 0.5% is consistent to what is expected and presented on the literature, lower than 2% for core $NaYF_4$:YbTm [2]. The nonlinear QY observed in the studied $NaYF_4$:YbTm might be directly related to the complex UC multi steps process. The UC in this material involves two different RE ions apart from each other inside the host lattice due to the low concentration of the dopants. In addition, the absorption/emission process relays on

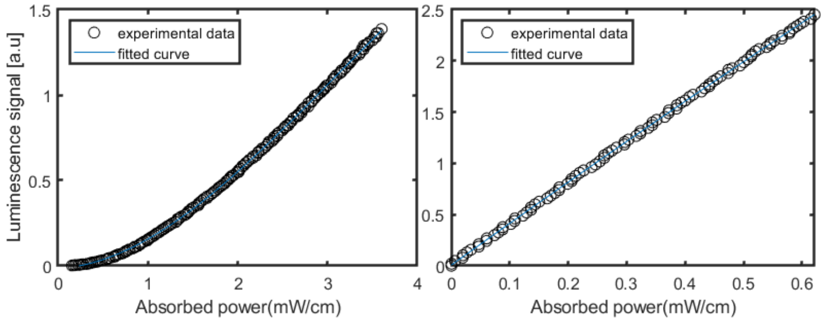


Figure 2: Luminescence signal against absorbed power. The NaYF4:Yb,Tm UCNP (left) presents a nonlinear behaviour, as a contrast, the DY-781 dye (right) shows a well known linear behaviour emitting more light as it absorbs.

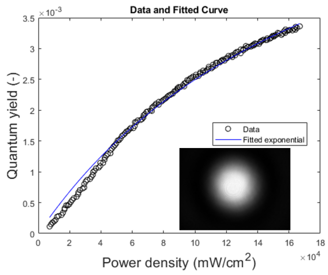


Figure 3: Nonlinear quantum yield as a function of the power density

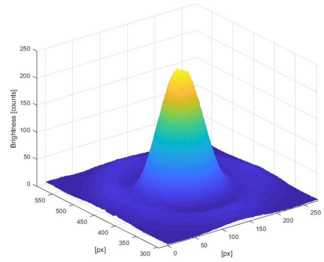


Figure 4: Gaussian beam profile used to excite the studied samples.

multiple photons absorption involving energy being transferred between ions. Therefore, a careful study is needed to explore the nature of this process.

Here we present only the QY curve for the emission at $800\ nm$, which corresponds to the 2 states energy transfer upconversion (ETU2). However this can be extended to other emission lines by appropriate selection of filtres on the emission paths and fluorescence calibration dye.

References

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