APPLICATION NOTE

Spectra, Lifetime and Quantum Yield of Upconversion Nanoparticles

AN_P91; Georgios Arvanitakis

Introduction

Photon upconversion (UC) is the conversion of two or more lower-energy photons into a higher-energy photon. An important type of upconversion material are upconversion nanoparticles (UCNPs), which are nanoparticles composed of rare-earth elements such as erbium and ytterbium embedded in a host matrix. UCNPs can be used to convert near-infrared light to higher energy light in the visible or ultraviolet region of the spectrum.

UCNPs have a vast range of potential applications. In solar energy harvesting, they can enhance the performance of photovoltaic devices and solar cell efficiency by converting unused solar spectrum segments into higher-energy photons. While in biomedicine UCNPs can be deployed for non-invasive imaging and diagnostics. As imaging contrast agents, they enable high-resolution imaging by converting infrared light into visible light, enabling deeper tissue penetration and reduced background signal. In drug delivery, their unique optical properties can be harnessed for the controlled release of therapeutic agents.[1]

Understanding the upconversion luminescence properties of UCNPs is crucial for tailoring their properties to specific applications and optimising performance. In this Application Note, an Edinburgh Instruments FS5 Spectrofluorometer was used for a complete upconversion luminescence characterisation of UCNPs comprising spectral, time-resolved, and quantum yield measurements.

Materials and Methods

The sample studied was NaYF4:Yb,Er UCNPs with a polyethylenimine (PEI) polymer coating dispersed in deionised water at a concentration of 10 mg/mL. The UCNP dispersion was held in a 10 mm × 10 mm quartz cuvette and characterised using an FS5 Spectrofluorometer. For excitation, the FS5 was equipped with a 2W 980 nm laser diode with a pulse modulation box (PM-2), enabling both CW and pulsed operation. For detection the FS5 was equipped with two photodetectors: a PMT-900 and PMT-1010 (FS5-NIR upgrade) and multichannel scaling (MCS) lifetime electronics. The PMT-900, with a spectral range of 200-900 nm, was used for spectral and lifetime measurements, while the PMT-1010, with its extended spectral range out to 1010 nm, was used for quantum yield determination. The sample cuvette was held in the SC-05 Standard Cuvette Module for spectral and lifetime measurements, and the SC-30 Integrating Sphere Module was used for quantum yield measurements.

Figure 1 Edinburgh Instruments FS5 Spectrofluorometer.

Upconversion Spectrum

First, the emission spectrum of the nanoparticles was acquired (Figure 2) using the 980 nm laser diode in CW mode for excitation and the PMT-900 for detection.

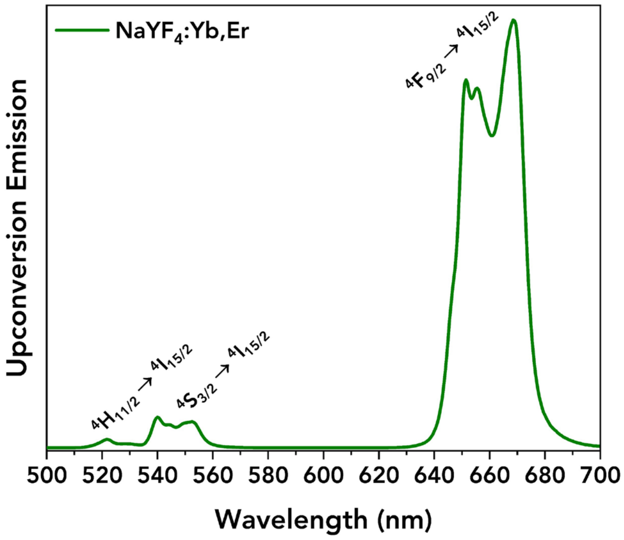

Figure 2 Upconversion emission spectrum of the UCNPs acquired using a 2 W 980 nm laser diode in CW mode and the PMT-900.

The emission spectrum can be used to identify the emissive energy transitions in the material. The emission arises from absorption of several low energy 980 nm photons by multiple Yb^{3+} ions (sensitisers), which transfer their energy to a single emissive Er^{3+} ion (emitter). The energy transfer takes place via a non-radiative multi-ion upconversion process. The emission peak centred around 660 nm is the ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}, while the additional emission peaks at 521 nm and 545 nm originate from the ${}^4H_{11/2} \rightarrow {}^4I_{15/2}$ and ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions respectively (Figure 3).[1,2]

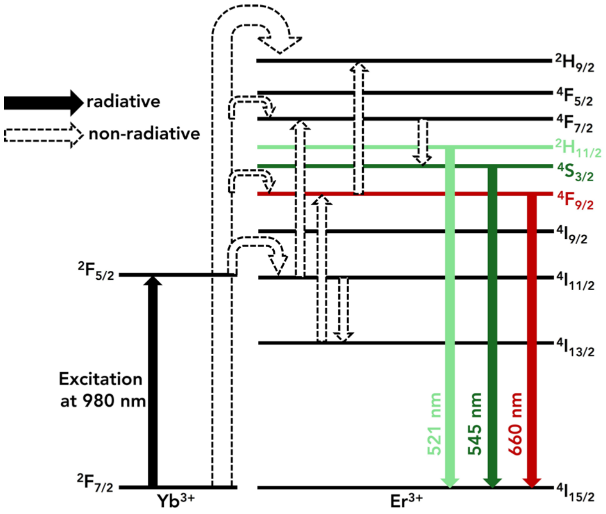

Figure 3 Energy level diagram showing the upconversion process within the NaYF$_4$:Yb,Er nanoparticles.

Upconversion Lifetime

The upconversion decay of the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition at 653 nm was then measured, Figure 4. The 980 nm laser diode was set to pulsed mode with a repetition rate of 500 Hz and a pulse width of 10 μs and the upconversion decay acquired using MCS single photon counting. The decay was then fitted in Fluoracle® using a two-exponential model, yielding an intensity average lifetime of 125 μs.

The lifetime is shorter than previous reports of similar materials, which showed lifetimes above 440 μs.[3] A potential explanation for the difference in the lifetime values is the deionised water used for dilution, the presence of which could introduce strong quenching effects, resulting in a reduction of the lifetime.

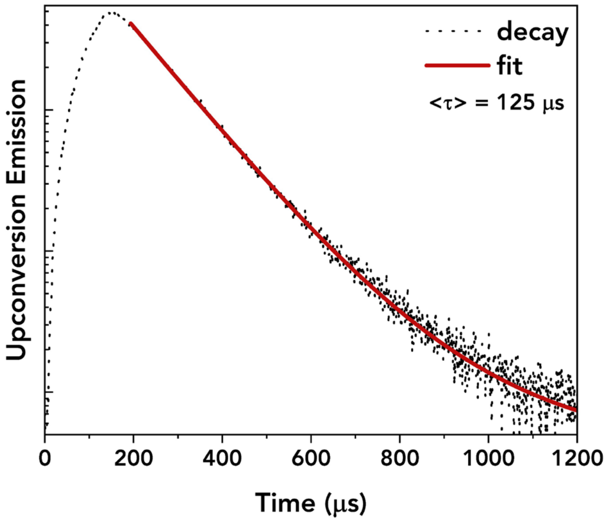

Figure 4 Upconversion decay of the UCNPs at 653 nm acquired using a 2 W 980 nm laser diode in pulsed mode at 500 Hz and the PMT-900.

Upconversion Quantum Yield

Measuring the quantum yield is critical for assessing the efficiency that UCNPs can generate upconverted light. UCNPs generally have lower quantum yields than their bulk counterparts. This is attributed to various factors such as the forbidden 4f – 4f transition, and inherent issues like poor crystallinity and surface defects.[4] The development of UCNPS with higher quantum yields is an ongoing research challenge.

To determine the upconversion quantum yield, the FS5 SC-30 Integrating Sphere Module was used. The SC-30 directly inserts into the FS5 with no alignment or optical fibres required. For light detection, the secondary PMT-1010 detector of the FS5 was used. The extended spectral range PMT-1010 to 1010 nm enables an accurate measurement of the 980 nm excitation light and is required for 980 nm excitation upconversion quantum yield measurements.

To determine the quantum yield, the emission and excitation scatter from the UCNP sample cuvette and from a reference cuvette containing deionised water only were measured in the SC-30. Figure 5 shows the emission and scattering peaks of the UCNPs and deionised water reference. The quantum yield was then calculated using the quantum yield wizard of the Fluoracle software which is based on the formula:

$$QY = \frac{E_{Sample} - E_{Reference}}{S_{Reference} - S_{Sample}} \times 100\% \qquad (1)$$

E is the integrated emission intensity, and S is the integrated scattering intensity. The quantum yield was calculated to be 0.014%. Such quantum yield values are typical for upconversion materials and are consistent with prior research.[4]

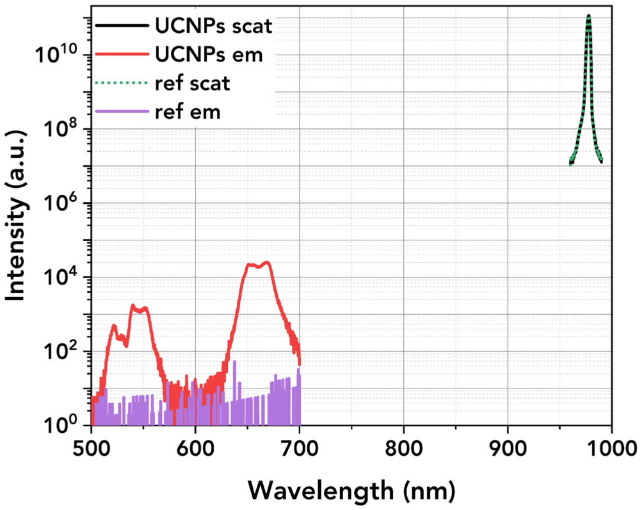

Figure 5 Scattering and emission spectra of the UCNPs sample and deionised water reference acquired using a 2 W 980 nm laser diode in CW mode and the PMT-1010.

Conclusion

This Application Note demonstrates a complete upconversion luminescence characterisation of upconversion nanoparticles using the Edinburgh Instruments FS5 Spectrofluorometer. The flexible source, detector and sample module upgrade options of the FS5 enables upconversion spectral, lifetime and quantum yield measurements to performed in a single compact instrument.

Acknowledgements

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References

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For more information, please contact:

+44 (0) 1506 425 300
sales@edinst.com
www.edinst.com