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A cost-effective quantum yield measurement setup for upconverting nanoparticles



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ABSTRACT

Generally, emission quantum yield values of upconverting nanoparticles are not reported, despite its importance for characterizing the material's performance, because the measurements require quite expensive setups (a single photomultiplier operating in a broad spectral regions from the visible to the near-infrared) and laborious procedures (spectral mismatch correction when two photomultipliers are used). Here we describe the implementation of a simple and cost-effective quantum yield measurement setup using a commercial integrating sphere-based spectrometer operating in the visible spectral range and a power meter to determine the incident number of photons. First, we validate the experimental methodology using well-known down-shifting standard phosphors (sodium salicylate and perylene). Then, we use the developed setup in an illustrative example of upconverting nanoparticles, SrF₂:Yb³⁺/Er³⁺ (20/2%), to quantify their emission quantum yield values in powder (0.0057 ± 0.0002 at 388 W cm^{-2}) and water suspension (0.0028 ± 0.0001 at 395 W cm^{-2}).

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1. Introduction

Photon upconversion refers to a nonlinear optical process characterized by the successive absorption of two or more pump low-energy photons (usually in the near-infrared, NIR, spectral region) followed by the emission at shorter wavelengths (higher energy) [1–3]. This unique form of spectral conversion [4,5] has received much interest in areas such as biological imaging [6–8], telecommunications [9], and photovoltaics [10–12].

The excited states of trivalent lanthanide ions (Ln³⁺) have lifetimes of up to several milliseconds enabling photon upconversion on Ln³⁺-doped materials even with a low-power continuous-wave (CW) laser. To fully evaluate the potential of upconverting materials, in particular nanoparticles, it is required the knowledge of the light output efficiency under a particular excitation wavelength and power density. The upconversion effectiveness may be accessed by the emission quantum yield (q) defined by the ratio between the number of emitted photons (N_e) and the number of absorbed ones (N_a), Eq. (1) [13,14]. Despite the emerging interest in Ln³⁺-doped upconverting nanocrystals and the recent availability of powerful and low cost NIR tunable CW laser diodes it is surprising to find so few publications in the literature dealing with the measurement of the emission quantum yield of these materials. Generally, the

experimental assessment of emission quantum yield values is rather laborious requiring the use of an integrating sphere, where the relevant data (absorbed pump laser and visible emitted intensities) are collected by a NIR sensitive photomultiplier tube (PMT) to collect the excitation photon density, and a PMT operating in the visible spectral range for the upconversion emission. Moreover, the large spectral shift between the emission and excitation wavelengths requires the combination of measurements originated in different detectors with spectral responsivity in the visible and NIR spectral ranges (to estimate N_e and N_a , respectively), requiring, therefore, a spectral mismatch correction [13,15–17].

Most of the emission quantum yield values already reported for upconverting nanoparticles refer to NaYF₄:Yb³⁺/Er³⁺ [15,16,18–22]. Depending on the synthesis method, solvent, particle's size and concentration, the measured values can vary almost two orders of magnitude [15,21]. Other example is M₂O₂S:Yb³⁺/Er³⁺ (M=Gd, Y, La) upconverting nanoparticles that at lower excitation power densities (up to 20 W cm^{-2}) display emission quantum yield values 3–4 times higher than those measured for NaYF₄:Yb³⁺/Er³⁺ (20/2%) [20]. Besides these examples of nanoparticles in suspensions, another intriguing one refers to LaF₃:Yb³⁺/Er³⁺ upconverting nanoparticles embedded into a sol-gel derived thin film. In this case, the experimental setup includes a NIR sensitive PMT (nitrogen cooled Hamamatsu R5509 with attenuation filters) to quantify the absorbed photons at 980 nm and a red-sensitive PMT (Peltier-cooled Hamamatsu R955) to measure the visible emission [23]. The response of both detectors was further scaled by using the overlap of

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the detection range (800–850 nm) and a scattering solution (LUDOX[®]). Although that the excitation power is not provided, the reported q value is $0.10 \pm 0.01\%$.

Here, we present a straightforward step-by-step method to estimate the emission quantum yield of upconverting nanoparticles from experimental data obtained using an integrating sphere without the need of spectral mismatch correction. For this purpose, we successfully designed a setup composed of a commercially available UV/visible spectrophotometer, an integrating sphere, a customizable excitation laser source emitting at 980 nm and a NIR sensitive power meter. The suitability of the methodology is demonstrated measuring the emission quantum yield values of well-known down-shifting standard phosphors, e.g., sodium salicylate and perylene, and NaYF₄:Yb³⁺/Er³⁺ (18/2%) upconverting nanoparticles. The values found are in excellent agreement with those already reported [21,24,25] and the method is used to measure the emission quantum yield value of SrF₂:Yb³⁺/Er³⁺ (20/2%) upconverting nanoparticles, both in powder and colloid form. Ln³⁺-doped SrF₂ nanoparticles gathered interest in recent years as upconverting ultraviolet emitters (Ln=Yb/Tm) [26] and for tissue visualization, (Ln=Yb/Er) [27] and (Ln=Nd) [28].

2. Materials and methods

2.1. Samples

The sodium salicylate (Merck P.A. 99.5%) was used as purchased and the perylene dye (Sigma-Aldrich, 97%) was suspended in cyclohexane (Sigma-Aldrich, anhydrous, 99.5%) with a concentration ranging from 4×10^{-2} – 4×10^{-4} M (0.25 – 0.0025 g L⁻¹). The detailed preparation of the sodium citrate capped SrF₂:Yb³⁺/Er³⁺ (20/2%) upconverting nanoparticles (average size ~40 nm) is reported elsewhere [29]. Water suspensions were prepared by using 2.5 mg of the nanoparticles in 1 mL, 2.0×10^{-2} M.

2.2. Methods

2.2.1. Photoluminescence spectroscopy

The photoluminescence spectra in the visible and NIR spectral ranges were recorded at room temperature with a modular double grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to R928 and H9170 Hamamatsu photomultipliers, respectively, using the front face acquisition mode. All the emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter.

The emission spectral radiant flux (or spectral radiant power), $S(\lambda)$, in units of W nm⁻¹, was measured at room temperature using an integrating sphere (ISP 150L-131, Instrument Systems) with a BaSO₄ coating and an internal diameter of 150 mm coupled to an array spectrometer (MAS-40, Instrument Systems) (Fig. 1). All the spectra were acquired with a resolution of 0.1 nm, 200 ms integration time, 5 averaged scans. The excitation sources consist of a multi-channel LED light source (MCLS, Ocean optics), emitting at 365 nm and 405 nm, and a NIR CW laser diode (PSU-H-LED, CNI Lasers), emitting a nearly Gaussian beam centered at 980 nm (TEM₀₀ mode, accordingly to the manufacturer). Acting on the laser driving current allows controlling the excitation power up to a maximum of 5.0 W. The excitation radiation is coupled into a customized optical fiber (SarSpec, 600 μm core diameter with an adaptable-length ferrule) that guides the excitation radiation to the sample compartment that consists of a quartz tube (outer diameter of 5 mm) placed at the entrance of the integrating sphere port. The fact that the sample is placed at the entrance of the port (Fig. 1) reduces reabsorption processes and avoids the sphere

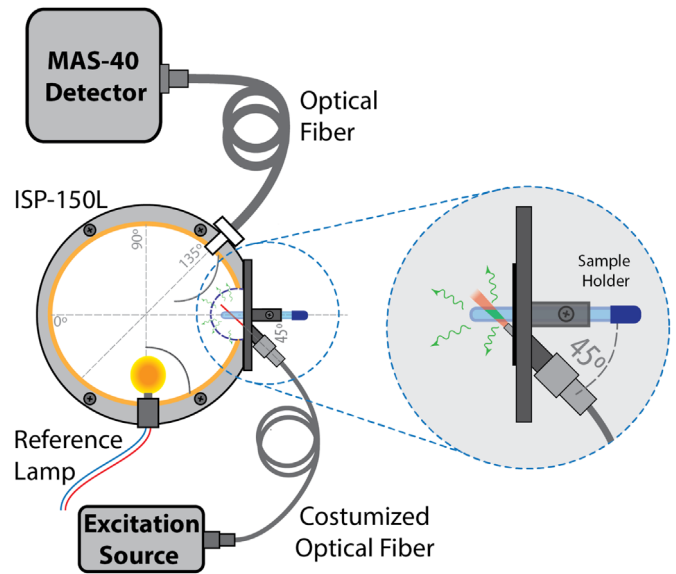


Fig. 1. Scheme of the experimental setup used to measure the emission quantum yields. The sample holder is illuminated using a customized optical fiber that guides the excitation radiation. The emission is collected by the ISP-150L integrating sphere and then guided through an optical fiber to the CCD of the MAS-40 detector, that quantifies $S(\lambda)$.

interior contamination [30], in comparison with the case in which the sample is placed at the center of the integrating sphere [13]. Prior to the measurements, the setup self-absorption correction was implemented using a reference lamp (ISP 150L-131, Instrument Systems). The incident optical power (in units of W) was measured with FieldMaxII-TOP (Coherent, 10 nW–1 W) (NaYF₄:Yb³⁺/Er³⁺ upconverting nanoparticles) and Thermopile-S310C (Thorlabs, 10 mW–10 W) power meters (sodium salicylate and SrF₂:Yb³⁺/Er³⁺ upconverting nanoparticles). The laser power density was computed using the ratio between the excitation power (measured at the exit of the customized optical fiber) and the illuminated area. The illuminated area is calculated using the numerical aperture of the fiber (0.22) and the characteristic geometrical arrangement of the setup (distances, angles, quartz wall thickness, Fig. 1).

2.2.2. Emission quantum yield

The emission quantum yield, q , given by:

$$q = \frac{N_e}{N_a} \quad (1)$$

requires the independent quantification of N_e and N_a . An integrating sphere coupled to a CCD enables the quantification of $S(\lambda)$ in the visible spectral range:

$$S(\lambda) = \frac{dP}{d\lambda} = \frac{d}{d\lambda} \left(\frac{dN}{dt} \frac{hc}{\lambda} \right) = \frac{hc}{\lambda} \frac{d}{d\lambda} \left(\frac{dN}{dt} \right) \quad (2)$$

where h and c denote the Planck constant and the speed of light in vacuum, respectively, dN/dt the photon flux per unit of time and λ the photon wavelength. The power P is given by the product of the number of photons by its energy. Thus, from the experimental measurement of $S(\lambda)$, the number of photons N (N_e or N_a) is determined by:

$$\frac{dN}{dt} = \frac{1}{hc} \int_{\lambda_1}^{\lambda_2} [S(\lambda) \lambda] d\lambda \quad (3)$$

where the integral limits correspond to the emission ($N=N_e$) or absorption ($N=N_a$) spectral ranges. Experimentally, N_a is the difference between the number of photons not absorbed by the

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