Supplementary Materials

Absolute Quantum Yield Measurements of Colloidal NaYF₄ Upconverting Nanoparticles

John-Christopher Boyer and Frank C. J. M. van Veggel

University of Victoria, Department of Chemistry, P. O. Box 3065, Victoria, British Columbia, Canada, V8W 3V6.

Synthetic Procedures

All chemicals utilized in the synthesis of the upconverting nanoparticles and bulk sample were purchased from Aldrich and used as received.

Synthesis of Bulk NaYF₄ material

The lanthanide trifluoracetate precursors were prepared from the corresponding lanthanide and yttrium oxides and trifluoroacetic acid (99%). In the case of the NaYF₄: $Er^{3+}2$ mol%, Yb³⁺20 mol% codoped sample, 9.6 mg (0.025 mmol) of Er_2O_3 , 98.5 mg (0.25 mmol) of Yb₂O₃, and 220.2 mg (0.975 mmol) of Y₂O₃were dissolved in 10 mL of 50% aqueous trifluoroacetic acid at 80 °C. The residual water and acid were then slowly evaporated at 80 °C. Subsequently, 0.3400 g (2.5 mmol) of sodium trifluoroacetate (98%) was added to the lanthanide trifluoroacetates and the powders were ground with a mortar and pestle. The resulting powder was heated to 110 °C in an oven and maintained at this temperature overnight to remove any residual moisture. The powder was then placed in a crucible and heated to a temperature of 400 i°C at a rate of 10 °C/min under air in a tube furnace and kept at this temperature for 4 hr. The furnace was then left to cool to RT. The resulting solid was then ground with a mortar and pestle to obtain a fine powder.

Synthesis of 10 nm NaYF₄ nanoparticles

The 10 nm NaYF₄: Er³⁺2 mol%, Yb³⁺20 mol% nanoparticle sample was synthesized using the synthetic procedure outlined in the following publication:

G. S. Yi and G. M. Chow, Advanced Functional Materials, 2006, 16, 2324.

No changes were made to the reported procedure.

Synthesis of 30 nm and 100 nm NaYF₄ nanoparticles

The 30 nm and 100 nm NaYF₄: $Er^{3+}2$ mol%, Yb³⁺20 mol% nanoparticle samples was synthesized using the synthetic procedures outlined in the following publications:

H.-S. Qian and Y. Zhang, Langmuir, 2008, 24, 12123.

Z. Li and Y. Zhang, *Nanotechnology*, 2008, **19**, 345606/1.

No changes were made to the reported procedures.

Synthesis of 30 nm NaYF₄ core/shell nanoparticles

The 30 nm NaYF₄: $Er^{3+}2$ mol%, Yb³⁺20 mol% / NaYF₄ core/shell nanoparticle sample was synthesized using the synthetic procedure outlined in the following publication:

H.-S. Qian and Y. Zhang, Langmuir, 2008, 24, 12123.

No changes were made to the reported procedures.

Powder X-ray Diffraction

Powder X-ray diffraction (XRD) data were acquired with a Rigaku Miniflex Diffractometer. Concentrated colloidals of the NaYF₄ nanoparticle samples in hexanes were drop-cast onto a zero-background holder and allowed to dry. Step-scan X-ray powder diffraction data were collected using a Rigaku Miniflex Diffractometer. A Cr radiation source was used at 30 kV and 15 mA with a K β filter, a 4.2° scattering slit, and a 0.3 mm receiving slit. XRD data was collected in the 20-140° (2 θ) range with a scanning step size of 0.02° (2 θ)and a counting time of 3 s per step.

Transmission Electron Microscopy

TEM was performed on the NaYF₄: $Er^{3+}2\%$, Yb³⁺20% nanoparticle samples using a Hitachi H-7000 microscope operating at 75 kV equipped with a charge-coupled device (CCD)-camera. A small amount of the sample (~1 mg) was dispersed in 1 g of hexane to give an approximate 0.1 wt% solution. One drop of the resulting nanoparticle dispersion was dropcasted on a formvar/carbon film supported on a 300 mesh copper grid (3 mm in diameter)and allowed to dry in air at room temperature.

Table S1. Raw data used for calculation of upconversion quantum yields for NaYF₄: $Er^{3+} 2 mol\%$, Yb³⁺ 20 mol% samples. The muber of *hv* Absorbed must be multiplied by 10000 to take into the account attenuation factor of the neutral density filter.

Samples	Power Density (W/cm ²)	Number of <i>hv</i> Emitted	Number of <i>hv</i> Absorbed
ErYb1	20	40989	132
ErYb2	150	26118	1154
ErYb3	150	16101	1321
ErYb4	150	428	1257
ErYb5	150	27916	1380



Figure S1. Photos of the experimental set-up showing the position of the diode laser and integrating sphere in the fluorimeter.



Figure S2. Experimental X-ray diffraction (XRD) patterns for NaYF₄: Er^{3+} 2%, Yb³⁺ 20% nanoparticleand bulk samples. Broad peak located at 30° is attributed to organic oleate layer.



Figure S3. Transmission Electron Microscopy (TEM) images of NaYF₄: $Er^{3+} 2\%$, Yb³⁺ 20% nanoparticles with average particle size of A) 10 nm, B) 30 nm, and C) 100 nm, respectively. D) TEM image of NaYF₄: $Er^{3+} 2\%$, Yb³⁺ 20% / NaYF₄ core/shell nanoparticles.