Thermal imaging of liquids using luminescent $NaYF_4:Yb^{3+},Er^{3+}$ nanoparticles.

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In the present work, a temperature gradient induced in water under external optical excitation is measured by using luminescent nanoparticles and confocal fluorescent microscopy. A pump-and-probe experiment, in an aqueous solution containing $NaYF_4:Yb^{3+},Er^{3+}$ nanoparticles, was designed for this purpose . Changes in a particular doublet emission of Er^{3+} ion are used to optically measure water temperature and temperature gradients. Temperature measurements in liquid solutions with sub-micrometer spatial resolution is a quite interesting and active research area.

For biomedical applications these thermal probes must be monodispersed in water. To date, many nano-temperature-sensitive compounds have been used as nano-thermometers. These compounds include metallic nanotubes, carbon nanotubes doped with gallium and a wide range of luminescent nanoparticles, such as $ZnS:Mn^{2+}$ or CdTe.

It appears very interesting to use dielectric nanocrystals codoped with Er^{3+} and Yb^{3+} as nano-sensors. This is because this couple of luminescent ions has a relatively high infrared to visible up-conversion luminescence efficiency by means of an effective $Yb^{3+}\rightarrow Er^{3+}$ energy transfer, and sharp emission lines due to acceptor Er^{3+} ion. In addition, the Yb^{3+} donor ion has absorption bands in the infrared, around 980nm, a wavelength that is in the so-called biological window.

To date, most of the studies in the field of temperature measurement with these nanocrystals have been limited to nanoparticles in powder form. However, $NaYF_4$ nanocrystals can be made monodispersed in liquids. Therefore they could be used as biocompatible nano probes. Properly coated, these nanoparticles are soluble in polar solvents, as water. We used this solvent also because the idea was to take advantage of the heat load experienced by water under an infrared excitation beam at 980nm. Such excitation beam would produce a thermal gradient related to the absorbed power profile that can be imaged by means of the Er^{3+} luminescence of the nanoparticles.

For this purpose, hydrophilic $NaYF_4$: Yb, Er (PEI-capped) nanoparticles (2 mol % Er^{3+}, 18 mol % Yb^{3+}) with an average size of 18 nm were synthesized by a solvothermal process. Then they were solved in of water (1% in weight) and the solution was excited by 980nm, a radiation which is also absorbed by the Yb^{3+} ions that subsequently transfer its excitation to the Er^{3+} ions. To measure the temperature dependence of the Er^{3+} emitted light, the sample was mounted on the top of a resistor connected to a thermocouple, so that we could monitor the sample temperature and, at the same time, the luminescence of the nanoparticles. The emitted light was sent to a monochromator (SPEX Industries model 500 M) followed by a CCD mark Synapse. Data were processed through the program LabSpec 5. In Figure 1 the Er^{3+} spectrum in the wavelength range 510-580nm is shown for two different temperatures. A change in the relative intensities of the 520nm ($^4S_{3/2}\rightarrow{}^4I_{15/2}$) and 540nm ($^2H_{11/2}\rightarrow{}^4I_{15/2}$) Er^{3+} bands occurs when increasing temperature. This change is due to a thermal redistribution in the population of the $^4S_{3/2}$ and $^2H_{3/2}$ excited states of Er^{3+} ions.

Figure 2 shows a semi logarithmic plot of the $\frac{I_{520nm}}{I_{540nm}}$ intensity ratio versus the reciprocal temperature ($\frac{1}{T}$). From this graph we have a temperature calibration of our system by means of the Er^{3+} luminescence.

Once we have calibrated our nano-thermometer the next step is to estimate the possibility of “gradient temperature measurements”. For this purpose a pump-probe experiment was designed. By one side, the sample was illuminated by a 1.7 W, 980nm tightly focused laser beam (“the pump”) that produces a thermal gradient due to a gradient in the light absorbed by water at the focal area. The left side of Figure 3 shows this gradient measured by means of a fluorescence intensity image. The intensity is higher in the focal volume of the pump laser beam and becomes smaller as far as we get away from it. Now, by using another laser resonant to the Er^{3+} ions (488nm, “the probe”) we were able to determine a temperature map as can be seen on the right side of Figure 3. In this map we can clearly appreciate the temperature gradient from the focal point (29º) and the non illuminate area (22º). This result is quite promising for measuring intracellular temperature variations.

References:

[1]. Boyer, J.C., et al., Journal of the American Chemical Society,**Synthesis of colloidal upconverting NaYF4 nanocrystals doped with Er3+, Yb3+ and Tm3+, Yb3+ via thermal decomposition of lanthanide trifluoroacetate precursors**. 2006. **128**(23): p. 7444-7445.

[2]. Fiore Vetrone et al. *ACS Nano (in press),* **Temperature Sensing at the Nanoscale using Fluorescent Nanothermometers**.

Figures:

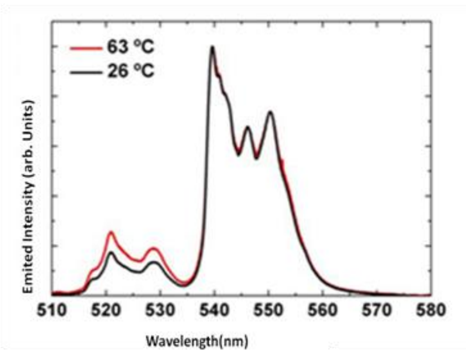

Figure 1. Upconversion emission spectra obtained at two different cuvette temperatures (I_{exc}=920nm)

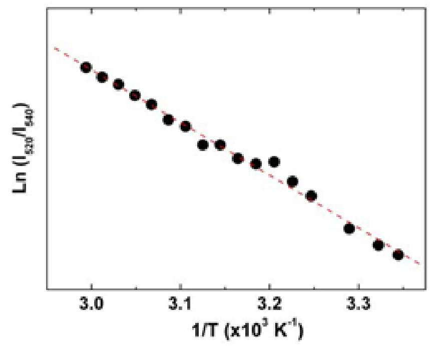

Figure 2. A plot of ln(I_{520nm}/I_{540nm}) vs. 1/T to calibrate the thermometric scale for the water dispersible $NaYF_4$:Er^{3+},Yb^{3+} nanoparticles.

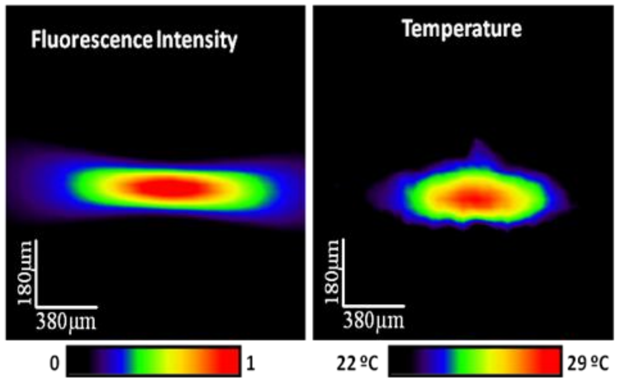

Figure 3. Right: Confocal image of the 980nm excited upconverted luminescence (pump absorbed profile). Right: Thermal image of the spot created by the 980nm pump profile