Ag/Ag_2S nanocrystals for high sensitivity near-infrared luminescence nanothermometry

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Measuring temperature of localized parts of the body has attracted a lot of attention recently due to the observation that temperature raise in certain areas is a symptom of diseases such as cancer, strokes or inflammation processes.[1] For this purpose, nanocrystals have been used as luminescence nanothermometers (LNThs) by monitoring the change in their photoluminescence (PL) properties with temperature. Current most sensitive LNThs consist on rare-earth doped nanostructures including core shell quantum dots (QDs) containing heavy metals like lead or cadmium.[2] We have identified silver sulfide (Ag_2S) nanocrystals as an optimum luminescent probe since they have proven to be non-toxic[3] and their PL falls in the range called second biological window (II-BW), where tissues show little absorption and autofluorescence, allowing higher signal to noise ratio.[4] We have carried out the synthesis and a thorough morphological, compositional and optical characterization including different high resolution transmission electron microscopy (HRTEM) and transient absorption spectroscopy (TAS) techniques. Our study shows that the as-synthesized NCs consist on a hybrid structure Ag/Ag_2S and their optical properties were found to be highly affected by temperature. The ability of these NCs for subtissue imaging and thermal sensing is tested by two simple experiments:

i) A NCs dispersion is spin coated onto a PET thin film (Fig 1a and 1b) and a sample of tissue of variable thickness is placed on it. The sample is heated using a high power laser and the read-out is used to obtain an image an a thermal reading.
ii) A NCs dispersion is injected in a tissue sample at different depths and the thermal reading is used to obtain the thermal diffusivity of the tissue.

The temperature-PL study shows a dramatic intensity quenching in the 15°C to 50°C range (up to 80% from 15°C to 35°C, Figure 1c) due to the increasing probability of non-radiative recombination with temperature and also a remarkable spectral red-shift of their PL. The change in these PL properties allows us to obtain thermal readings with a sensitivity of 4%·C^{-1} in the case of the intensity based analysis and of 2%·C^{-1} in the spectral change approach. The tissue diffusitivity obtained by the PL signal is in good agreement with previous results.

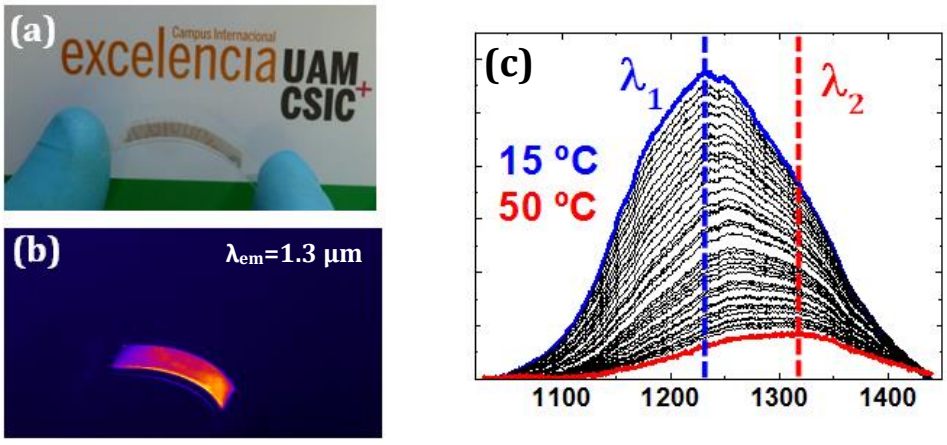

Fig. 1 a) Optical and b) infrared fluorescence of a flexible Ag/Ag_2S NCs thin film. C) Emission spectra of the NCs thin film from 15°C to 50°C.

1) E.Y.-K. Ng. *Int. J. Therm. Sci.,* **2009**, *48*, 849.
2) E. N. Cerón *et al.*, *Adv.Mat.*, **2015**, *27*, 4781.
3) M.-Y. Qin *et al*., *Nanoscale, **2015,** 7,* 19484.
4) S. Diao *et al*., *Nano Res*, **2015**, *8,* 3027.