

Lanthanide activated fluoride nanoparticles as luminescent probes and optical thermometers

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Lanthanide (Ln^{3+})-doped fluoride nanoparticles (NPs) present impressive luminescent properties, making them interesting luminophores for many technological applications as sensors, as well as diagnostic probes in nanomedicine^[1-3].

In this communication, we focus on alkaline-earth fluoride, as CaF_2 , SrF_2 and KY_3F_{10} NPs, properly activated with luminescent Ln^{3+} ions (e.g. Nd^{3+} , Tm^{3+} , Er^{3+} and Yb^{3+}). These nanomaterials show strong upconversion as well as downshifting emissions in the optical range, upon visible or Near Infrared (NIR) laser excitation. The NPs preparation directly in colloidal form has been investigated, by exploiting a “green chemistry”, microwave (MW) assisted hydrothermal technique and by using hydrophilic and biocompatible capping agents. The coordination of these capping molecules on the NPs surface confers excellent colloidal chemical stability in water-based dispersions. Moreover, more complex core@shell structured NPs, with different Ln^{3+} doping between the core and shell, have been prepared, by implementing the same MW assisted method.

Detailed luminescent properties of the NPs in the UV, visible and NIR regions upon laser excitation will be illustrated, putting also emphasis on how the core@shell structure impacts on the luminescence efficiencies in colloidal water dispersions. Particular attention will be devoted to describe the energy transfer processes among the different Ln^{3+} ions as Yb^{3+} or Nd^{3+} (sensitizers) and Er^{3+} , Tm^{3+} and Nd^{3+} (activators). Finally, the optical thermometric features of the presented colloidal NPs will be illustrated, in particular exploiting emissions within the biological windows. To this purpose, ratiometric calculation methods have been applied, using emissions coming from the same or different lanthanide ions.

References

- [1] C. Cressoni, F. Vurro, E. Milan, M. Muccilli, F. Mazzer, M. Gerosa, F. Boschi, A. Spinelli, D. Badocco, P. Pastore, N. Fernandez Delgado, M. Herrera Collado, P. Marzola and A. Speghini, *From Nanothermometry to Bioimaging: Lanthanide-Activated KY_3F_{10} Nanostructures as Biocompatible Multifunctional Tools for Nanomedicine*, ACS Appl. Mater. Interfaces, 2023, 15, 12171.
- [2] G. Lucchini, A. Speghini, P. Canton, F. Vetrone and M. Quintanilla, *Engineering efficient upconverting nanothermometers using Eu^{3+} ions*, Nanoscale Adv. 2019, 1, 757.
- [3] P. Cortelletti, A. Skripka, C. Facciotti, M. Pedroni, G. Caputo, N. Pinna, M. Quintanilla, A. Benayas, F. Vetrone and A. Speghini, *Tuning the sensitivity of lanthanide-activated NIR nanothermometers in the biological windows*, Nanoscale, 2018, 10, 2568.