

Área: MAT

Multifunctional Nanohybrids: Engineering Rare-earth-based Magnetic-Luminescent Platforms for Advanced Biomedical Applications

André L. Costa (PG),^{1,2} Airtón G. Bispo-Jr (PQ),³ Sergio A. M. Lima (PQ),^{1,2} Flavia Artizzu (PQ),⁴ Ana M. Pires (PQ)^{1,2}.

andre.lucas-costa@unesp.br

¹Chemistry and Biochemistry Department, São Paulo State University (UNESP), School of Technology and Sciences, Presidente Prudente, SP, Brazil; ²São Paulo State University (Unesp), Institute of Biosciences, Humanities and Exact Sciences, São José do Rio Preto, SP, Brazil. ³University of São Paulo (USP), Institute of Chemistry, São Paulo, Brazil. ⁴Department of Sustainable Development and Ecological Transition, University of Eastern Piedmont, Vercelli, Italy.

Keywords: Multifunctional Nanomaterials, Bioimaging and Therapy, Upconversion, Magnetic Nanoparticles, Nanobiotechnology.

Highlights

Multifunctional chemical platforms based on magnetic and luminescent core@multishell nanohybrids for biomedical applications¹. Advanced magnetic properties and cellular imaging capabilities. Lanthanide(III)-based near-infrared excitation that minimizes autofluorescence and cellular damage².

Abstract

The advancement in the development of multifunctional nanomaterials has driven new approaches for tumor diagnosis and treatment, integrating bioimaging and magnetic properties. Among these approaches, multifunctional chemical platforms stand out by incorporating different properties within a single material, enabling simultaneous applications in therapy and diagnosis. These platforms are highly relevant today, as they offer more effective and less invasive solutions for various medical conditions, promoting greater selectivity and efficiency in treatments^{1,2}. Furthermore, their versatility allows adaptations according to therapeutic needs, making them promising tools in biomedical nanotechnology. In this context, series of hybrid magnetic and luminescent core@multishell systems contain rare-earth ions (RE) were synthesized, to optimize their chemical, magnetic, and luminescent properties for biomedical applications. The materials consist of Fe₃O₄ nanoparticles (core) coated with a Y₂O₃:RE³⁺ layer (RE³⁺ = Tm³⁺, Yb³⁺), followed by a second shell of dense silica functionalized with carboxylate groups. This surface enables the anchoring of luminescent complexes [TR(β-diketonate)₃] (TR³⁺ = Eu³⁺), tuning their optical properties. The choice was for the Yb³⁺/Tm³⁺ pair to induce the upconversion phenomenon based on near-infrared (NIR) excitation. This reduces autofluorescence and cellular damage, thereby enabling more efficient imaging. The formation of the target phases was confirmed by X-ray diffraction. Vibrational infrared spectroscopy highlighted metal-oxygen bonds (ν(Y–O) and ν(Fe–O)), as well as interactions with silanol groups and Si–O–Si linkages. A preliminary study confirms that all the synthesized structures satisfactorily respond to an external magnetic field. Luminescence analyses revealed characteristic excitation and emission spectra of Eu³⁺, confirming the efficiency of the organic ligand in sensitizing this ion via the well-known "antenna effect". In the Fe₃O₄@Y₂O₃:Yb³⁺,Tm³⁺@SiO₂ with luminescent europium complex anchored on the silica surface, excitation with a 980 nm laser resulted in the Tm³⁺ upconversion emission with bands at 450–480 nm (¹G₄→³H₆), and 650 nm (¹G₄→³F₄). The presence of Yb³⁺ enhanced Tm³⁺ emission, demonstrating its role in sensitizing Tm³⁺ upconversion and validating the proposed material architecture. The obtained results highlight the feasibility of the synthesized nanohybrids for innovative biomedical applications, combining cellular imaging and magnetic properties within a single platform. Emission in the UV region enables subsequent excitation of Eu³⁺ complexes, expanding the potential for simultaneous therapeutic and diagnostic applications. These advances further emphasize the significance of materials engineering in the development of multifunctional nanoplatforms for oncology.

¹CUI, Xianjin et al. Synthesis, characterization, and application of core-shell Co_{0.16}Fe_{2.84}O₄@NaYF₄(Yb,Er) and Fe₃O₄@NaYF₄(Yb,Tm) nanoparticle as Trimodal (MRI, PET/SPECT, and optical) imaging agents. *Bioconjugate Chemistry*, v. 27, n. 2, p. 319-328, 2016.

²ZHENG, Bingzhu et al. Rare-earth doping in nanostructured inorganic materials. *Chemical Reviews*, v. 122, n. 6, p. 5519-5603, 2022.

Acknowledgments

FAPESP (2019/26103-7), CNPq (309448/2021-2 and 308868/2022-6), CAPES (Grant number 88887.686388/2022-00).