Bifunctional optical and magnetic nanocomposites containing Fe_3O_4 grafted inorganic matrices and functionalize with RE^{3+} complexes

L.U. Khan[1], D. Muraca[2], H.F. Brito[1], O. Moscoso-Londoño[2], M.C.F.C. Felinto[3], K.R. Pirota[2], E.E.S. Teotonio[4], O.L. Malta[5]

[1]*Department of Fundamental Chemistry, Institute of Chemistry, University of Sao Paulo, Av. Prof. Lineu Prestes, 748, 05508-000, São Paulo-SP, Brazil.*
[2]*Institute of Physics "Gleb Wataghin", Condensed Matter Physics Department, State University of Campinas (UNICAMP), 13083-859 Campinas-SP, Brazil.*
[3]*Nuclear and Energy Research Institute (IPEN-CQMA), Av. Prof. Lineu Prestes, 2242, 05508-000, São Paulo-SP, Brazil.*
[4]*Department of Chemistry, Federal University of Paraiba, 58051-970 João Pessoa-PB, Brazil.*
[5]*Department of Fundamental Chemistry, Federal University of Pernambuco, 50670-901, Recife-PE, Brazil*

The design of bifunctional magnetic luminescent nanomaterials containing Fe_3O_4 functionalized with rare earth ion complexes of calixarene and β-diketonate ligands is reported. Their preparation is accessible through a facile onepot method. These novel Fe_3O_4@calix-Eu(TTA) (TTA = thenoyltrifluoroacetonate) and Fe_3O_4@calix-Tb(ACAC) (ACAC = acetylacetonate) magnetic luminescent nanomaterials show interesting superparamagnetic and photonic properties. Besides, the preparation of bifunctional nanocomposites, co-assembling photonic (RE^{3+}) and magnetic (Fe_3O_4) features into single entity nanostructures is reported through a facile method, using Fe_3O_4 as core nanoparticles, which were coated with SiO_2 shell and further grafted with Eu^{3+} and Tb^{3+} complexes. The sophisticated structural features and morphologies of the core-shell Fe_3O_4@SiO_2-(TTA-RE-L) nanomaterials were studied by SAXS analysis.

The core mean size $\langle D_{SAXS} \rangle$, shell thickness ΔR, cluster size ξ and fractal dimension D_F were determined by fitting the experimental SAXS data, corroborating through Transmission Electron Microscopy images. The DC magnetic properties at temperatures of 2 and 300 K were explored in support to the structural conclusions from SAXS and TEM analyses. The magnetic contributions of the RE^{3+} ions to the magnetizations of the Eu^{3+} and Tb^{3+} nanocomposites were discussed. The photoluminescence properties of the Eu^{3+} and Tb^{3+} nanocomposites based on the emission spectral data and luminescence decay curves were studied (Fig.1). The experimental intensity parameters (Ω_λ), lifetimes (τ), emission quantum efficiencies (η) as well as radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates were calculated and discussed, in addition, the structural conclusions from the values of the 4f-4f intensity parameters in the case of the Eu^{3+} ion. These novel Eu^{3+} and Tb^{3+} nanocomposites may act as red and green emitting layers for magnetic and light converting molecular devices.

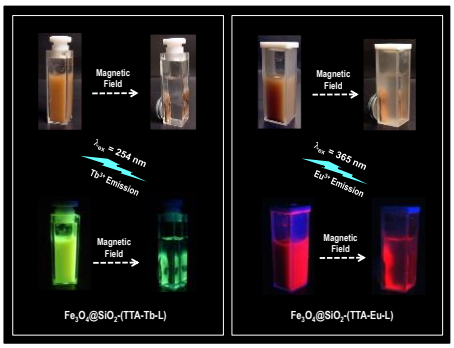

Fig. 1. Photographs of the Fe_3O_4@SiO_2-(TTA-RE-L), (RE: Eu and Tb) nanocomposites.

[1] Khan, L.U.; Brito, H.F.; Hölsä, J.; Pirota, K.R.; Muraca, D.; Felinto, M.C.F.C.; Teotonio, E.E.S.; Malta, O.L. *Inorg. Chem.*, **53** (2014) 2902.
[2] Khan, L.U.; Muraca, D.; Brito, H.F.; Moscoso-Londoño, O.; Felinto, M.C.F.C.; Pirota, K.R.; Teotonio, E.E.S.; Malta. O.L. J Alloys and Compd., 686, 453–466 (2016).

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