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Luminescent properties of hybrid materials prepared by the polymeric precursor method

Larissa H. Oliveira [a,*], Ana Paula de Moura [a], Elson Longo [a], José A. Varela [a], Ieda L.V. Rosa [b]

[a] LIEC-UNESP, Institute of Chemistry, Caixa Postal 355, 14800-900 Araraquara, SP, Brazil
[b] LIEC-UFSCar, Department of Chemistry, Caixa Postal 676, 13560-905 São Carlos, SP, Brazil

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ABSTRACT

Rare earth complexes (RE) can be incorporated in silica matrixes, originating organic/inorganic hybrid materials with good thermal stability and high rare earth emission lines. In this work, the hybrid material was obtained by the polymeric precursor method and ultrasonic dispersed with spherical silica particles prepared by the Stöber Method. The Raman spectra indicated that the Eu^{3+} ions are involved in a polymeric structure formed as consequence of the chelation and polyesterification reactions of this ion with citric acid and ethylene glycol. After the ultrasonic stirring, 2-hydroxynicotinic ligand will also compose this polymeric rigid structure. The TGA/DTA analysis showed that this polymeric material was thermal decomposed at 300 °C. Moreover, this process allows the chelating process of the 2-hydroxynicotinic acid ligand to the Eu^{3+} ions. The ^{29}Si NMR showed that the ultrasonic dispersion of the reactants was not able to promote the functionalization of the silica particles with the 2-hydroxynicotinic acid ligand. Moreover, heat treatment promotes the $[Eu(HnicO_2)_3]$ complex particles incorporation into silica pores. At this temperature, the TGA curve showed that only the thermal degradation of ethylene glycol and citric acid used during the experimental procedure occurs. The silica and hybrid materials are composed by spherical and aggregated particles with particle size of approximately 450 nm, which can be influenced by the heat treatment. These materials also present an absorption band located at 337 nm. The photoluminescent study showed that when the hybrid samples were excited at 337 nm wavelength, the ligand absorbs the excitation light. Part of this energy is transferred to the Eu^{3+} ion, which main emission, $^5D_0 \rightarrow {}^7F_2$, is observed in the emission spectrum at 612 nm. As the heating temperature increases to 300 °C, the energy transfer is more favorable. The lifetime values showed that the Eu^{3+} emission is enhanced due to the energy transfer process in the powders.

1. Introduction

The importance of rare earth elements is because of its particular luminescent properties, such as long lifetime and narrow emission lines. Thus, these elements can be employed in a broad range of applications, mainly including cathode ray tubes (CRTs), lasers and luminescent lamps [1]. On the other hand, the weak and narrow absorption bands of these lanthanides ions difficult its direct excitation process. In order to overcome this problem, the lanthanide ions, for example Eu^{3+} and Tb^{3+}, can be chelated with organic ligands. These molecules can also shield the metal ion from deleterious luminescence quenching interactions by O—H oscillators from solvent molecules [2]. The luminescence of these ions is obtained through the intramolecular energy transfer from excited state of the ligand to the emitting level of the lanthanide ion. This phenomenon is knowledge as "antenna effect" [3,4].

The factors such as poor stabilities under high temperature or moisture conditions and low mechanical strength limit their practical use. Thus, lanthanide complexes can be embedded into solid surfaces. When incorporated, its properties can be modified by interactions between the matrix and these organic complexes [5–7]. In this way, Langmuir–Blodgett films [8], porous glasses [9], oxide surfaces [10], and sol–gel glasses [11], has been applied as hosts to embedded many lanthanide ions. Among them, silica is one of the most inorganic substances used as support for several systems due to its easiness to control size and shape of particles, and also to control volume and pore size distribution as well as surface area, when compared to other metals such as titanium, zirconium or aluminum [12].

The sol–gel technique can be a suitable wet chemical route to synthesize lanthanide silica-based organic/inorganic hybrid material due to mild synthetic condition and processing versatile. The incorporation of lanthanide complexes into silica gel matrix, which

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* Corresponding author. Address: LIEC-UNESP-Instituto de Química, Rua Francisco Degni, 55, CP 676 CEP 14800-900, Araraquara, SP, Brazil. Tel.: +55 16 33519828x9894.

E-mail address: larissahelena2009@gmail.com (L.H. Oliveira).

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is based on hydrolysis and polycondensation reactions, give rise to multifunctional materials allowing the formation of direct chemical bonds between the organic and inorganic components and, furthermore, it is possible to tune its optical properties [13–15].

However, there are some drawbacks like low stability and solubility of the complexes at the low pH needed for the hydrolysis reaction, the cracking of the materials during the drying period and the presence of water molecule in the silica pores. Thus, polymers molecules can be introduced into these materials to solve this problem. Generally, the most used polymers containing carbonyl groups are Polyvinyl butyral (PVB), Polyvinylpyrrolidone (PVP) and Polymethylmethacrylate (PMMA). Firstly, these groups are grafted onto silica microsphere by means of Si—O bonds, then, the lanthanide complexes are introduced above the system polymer-SiO_2 through their coordination reaction resulting in a rigid hybrid system [16–18].

Based on the papers published in the last years, the polymeric precursor method has been chose to synthesized hybrid materials, in this study. These investigations were encouraged by the possibility to control the homogeneity of the systems in molecular level as well as the production of particles with uniform size in a reactional procedure at low temperature. Moreover, using this methodology, the organic reagents used during the synthesis can be decomposed by the thermal treatment used. Besides that, hybrid materials can be synthesized in a shorter period of time (~2 h) when compared to other systems like EDTA-Ln-TTA-SiO_2 where Ln = Eu, Tb and Gd [19].

The silica-based hybrid materials can be classified according to its composition, nature of interactions or chemical bonds involved: The Class I hybrid material concerns the conventional doping systems in which only weak interactions, such as hydrogen bonding, van der Waals forces and/or weak static effects, exists between the organic and inorganic components. In the Class II hybrid material, the organic and inorganic components are covalently linked [20,21]. Recently, several organic ligands have been used in the obtention of silica-based hybrid materials, such as terpyridine [22], 1,10-fenantroline [23], bypyridine [3] and dicarboxilic acids [24,25]. The heretocyclic 2-hydroxynicotinic acid ligand, shown in Fig. 1, is a heterocyclic ligand which has been widely used for synthesizing transition metal ion complexes [26–28]. This organic ligand exhibit enol–keto tautomerism transformation in the solid state and in solution, due to the mobility of the unstable hydrogen atom of the OH group, giving rise to different coordination modes of $HnicO^-$ including monodentade, bridging, N,O-chelating, and O,O-chelating that could result in a large diversity of coordination compounds, as described elsewhere [29].

The luminescent properties of these materials showed that an intramolecular energy transfer from the organic ligand to RE ions is involved, and also shows the promising applications that these classes of materials are therefore expected in nano-technological fields. Thus, in this present paper, a lanthanide silica based organic/inorganic hybrid material was prepared by the polymeric precursor method [30], where the spherical silica particles was employed as host inorganic matrix, and the lanthanide complex formed between the heterocyclic ligand 2-hydroxynicotinic acid (H_2nicO) and Eu^{3+} ion composed the organic component. These hybrid materials were characterized by Fourier transform Raman spectroscopy (FT-Raman), thermal analysis (TGA/DTA), field emission scanning electron microscopy (FE-SEM), ^{29}Si Nuclear magnetic ressonance spectroscopy (^{29}Si NMR). The photophysical properties were investigated through the Uv–vis absorbance spectroscopy and by the excitation and emission spectra of the Eu^{3+} ion as well as its lifetime in ms.

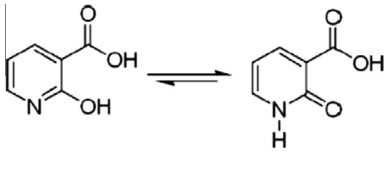

Fig. 1. Molecular structure and enol-ketone tautomeric mechanism of the 2-hydroxynicotinic (H_2nicO) ligand [20].

2. Experimental section

2.1. Synthesis of the spherical silica particles

The Stöber Method [31] was employed in the synthesis of the spherical silica particles, which is based on the hydrolysis of the TEOS catalyzed by the ammonia. An amount of ethanol and TEOS was stirred for some minutes. To this solution were quickly added ethanol, ammonia and deionized water. The recipient was hermetically closed and stayed under stirring for more 4 h. After that, the solvent was evaporated and the solid obtained was dried in a furnace at 100 °C for 12 h, where it was obtained 2.54 g of spherical silica.

2.2. Synthesis of the hybrid materials

The resin used for synthesize the hybrid materials was prepared by the polymeric precursor method [32] using an aqueous Eu^{3+} citrate solution prepared from europium nitrate (europium oxide in nitric acid) and citric acid. The citric acid/Eu^{3+} ratio was fixed at 3:1 (mol%). Ethylene glycol was added to the citric acid solution using a mass ratio (citric acid/ethyleneglycol) of 40:60. The Eu^{3+} complex organic phase onto the spherical SiO_2 surface was prepared by a wet and soft chemical method [33]. An amount of 1.0 g of spherical SiO_2 was added in 25 mL of deionized water and then sonicated for 5 min. An aqueous solution containing the 2-hydroxynicotinic acid ligand (pH 6.0) was also prepared. The resin containing Eu^{3+} ions was mixed to the aqueous solution with the organic ligand. Afterwards, the solution was dispersed on the spherical SiO_2 aqueous solution and then sonicated for 5 min. The solvent was evaporated to obtain the SiO_2-[Eu(HnicO)] sample, and then was dried at 100 °C for 12 h resulting the Hybrid I and 300 °C for 2 h giving rise to Hybrid II using a heating rate of 5 °C/min.

2.3. Synthesis of the lanthanide complex

Firstly, a $Eu(NO_3)_2 \cdot nH_2O$ solution was prepared by dissolving 0.01 mol of Eu_2O_3 in HNO_3 under stirring. The lanthanide complex were prepared by adding aqueous solution (5 mL) of the respective lanthanide salt ($Eu(NO_3)_2 \cdot nH_2O$) to an aqueous solution (15 mL, pH 6.0) of 2-hydroxynicotinic acid. The ligand quantity added to the lanthanide salt solution was measured using a RE ion/ligand ratio of 1:3 mol. After stirring the mixture for same minutes a white powder started to precipitate in the beaker. The powder was filtered and dried at 100 °C for 12 h. This experimental procedure is in accordance to describe in Ref. [34].

2.4. Characterization

The powder morphologies were verified using a scanning electron microscope (Jeol JSM-7500F microscope). Fourrier transform Raman data were obtained at room temperature using a RFS/100/S Bruker FT-Raman equipment with spectral resolution of 4 cm^{-1} attached to a Nd:YAG laser, promoting an excitation light of 1.064 nm in the frequency range of 500 up to 3500 cm^{-1}. The ^{29}Si NMR spectra were collected in a VARIAN Unity 400 spectrophotometer operating in 79.5 MHz with a high efficient decoupling using a scanning in the room temperature. For acquisition of the ^{29}Si NMR spectra was used a zirconium oxide rotor of 7 mm diameter and 6 kHz speed and the magic angle speed technique (MAS) with a recycle of 0.3 s between 90° pulses was also performed. The thermal analysis was recorded in Netzsch-Thermische Analyse STA 409 cell equipment using a heating rate of 5 °C/min and synthetic air atmosphere. Ultraviolet visible absorption spectra of the as-prepared materials were performed using Cary 5G equipment. The emission and excitation spectra of these samples were obtained under a 450 W xenon lamp source in a JOBIN YVON SPEX TRIAX 550-FLUOROLOG III spectrofluorometer at room temperature. Lifetime data of the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ transition of the $[Eu(HnicO_2)_3]$ complex, Hybrid I and Hybrid II powders were evaluated from the decay curves using the emission wavelength set at 613 nm and excitation wavelength set at 393 and 337 nm.

3. Results and discussion

3.1. Fourrier transform Raman (FT-Raman)

Fig. 2 presents the FT-Raman spectra of the free ligand (a), $[Eu(HnicO_2)_3]$ complex (b) Hybrid I (c) and Hybrid II (d) powders.