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Optical properties of Eu-doped hybrid materials prepared from dimethyl and methyl alkoxides precursors

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ABSTRACT

The sol–gel methodology allows for the attainment of hybrids with controlled doping, which cannot be achieved via other methods. In this work, a europium (III) dipicolinate complex has been incorporated into hybrid materials prepared from alkoxides modified with methyl groups, obtained via the sol–gel process, aiming at the preparation of hydrophobic hybrids. The photoluminescence analysis showed that the europium (III) complex was not affected during its incorporation into the hybrid materials, since its spectroscopic properties were maintained. The X-ray diffraction analysis revealed that the synthesized silica was amorphous, whereas the alkoxides dimethyldimethoxysilane and methyltriethoxysilane displayed diffraction halos centered at $2\theta = 10^{\circ}$, which disappeared after heating, as well as halos centered at $2\theta = 20^{\circ}$, typical of silica. The scanning electron microscopy analysis provided evidence of different morphologies for the hybrids. The thermal analysis demonstrated variations in the curves of the hybrids prepared with europium (III) chloride and those obtained in the presence of the europium (III) dipicolinate complex.

1. Introduction

Hybrid materials have attracted the attention of materials chemistry researchers since the 1980s. Due to the advancements in the use of mild synthetic conditions in inorganic chemistry, mixing organic and inorganic components at the nanometric scale has become possible at virtually any ratio [1,2]. The sol–gel method has been very frequently employed in the area of materials science, because it offers the possibility of carrying out reactions under mild conditions such as relatively low temperature. Moreover, this methodology allows for the utilization of metallo-organic precursors, the preparation of nanocrystalline materials with high porosity, and the control of the ageing and drying conditions. As a consequence, materials with controlled pore size and enhanced mechanical resistance as well as high optical quality are achieved, not to mention that thin films, fibers, monoliths, or amorphous solids can be obtained [3–8].

Hybrid materials can be broadly defined as synthetic materials containing intimately mixed organic and inorganic components. This mixture yields a synergy that provides these materials with unique features and an array of unprecedented properties (mechanical, optical, electronic, chemical, and thermal, among others) just by careful selection of the organic and inorganic components and the appropriate choice of conditions for their joint processing [1, 9–10]. Nowadays, hybrid materials play a key role in the development of several functional systems in the areas of catalysis, optoelectronics, magnetic devices, dyes and coatings, fire-retardant chemicals, full cells, biohybrids, among others [11–13].

The interest in the optic and photonic applications of hybrids materials has existed for over 20 years. The versatility of the sol–gel process offers a large range of possibilities for the preparation of these materials. The organic dye that is incorporated in the silica matrix by sol–gel preserves its optical properties [14]. The lanthanide ions have been employed as precursors of luminescent materials in several applications, but the lanthanides complexes are promising for the production of efficient light conversion molecular devices for use as luminescent labels for fluoro-immunoassays, as light concentrators for photovoltaic devices, and as antennae in photosensitive bioinorganic compounds and high-technology optics [15].

Luminescent lanthanide ions present optical properties that are attractive because of the high-purity degree of the emitted color and of the fine emission lines that arise as a consequence of the electronic transitions taking place within the partially filled 4f layer. The f–f transitions responsible for the optical transitions are usually characterized by long lifetimes, which range from microseconds to milliseconds [16–18]. The growing interest in the preparation of organic–inorganic hybrids by the sol–gel route stems from the fact that lanthanide ions can be incorporated into

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these materials at different ratios, while their luminescent properties are maintained. The luminescence obtained by direct excitation of the lanthanide ion is little efficient, since these ions do not exhibit high molar absorptivity. However, this difficulty can be easily overcome by using compounds containing organic ligands. The latter serve as sensitizers of the lanthanide ion emission, once they can absorb light and transfer it to the ion, which in turn emits the luminescence. In this way, there is an intramolecular energy transfer from the ligand to the central metal ion, a phenomenon known as the antenna effect [16,19,20]. The presence of organic molecules serving as ligands not only enhances the light intensity of the emission, but it also hinders undesirable interactions taking place between the ions and the water molecules, which could lead to energy loss from the excited states via vibrational modes and consequent luminescence suppression [21,22].

The use of lanthanide complexes in hybrid matrices for enhancement of the luminescence of the ion alone has been the object of study of many investigators, owing to their potential application in photonic crystals, optical glasses and fluorescent systems, or lasers. The sol–gel method allows for the incorporation of these complexes without risking their decomposition [20,23,24]. Among the various organic ligands employed in the synthesis of lanthanide ion coordination compounds, countless works using tridentate ligands derived from dicarboxylic acids have been published [22,25–30].

In this paper, hybrid materials containing tetraethylorthosilicate alkoxides (TEOS), dimethoxydimethylsilane (DMDMS), and methyltrimethoxysilane (MTMS) doped with europium (III) chloride and/or the europium (III) dipicolinate complex have been prepared. The ligand dipicolinic acid (dpa) has been selected because it is a diacid that promotes europium (III) ion emission via the antenna effect [31,32].

2. Experimental section

2.1. Preparation of the hybrids

The hybrids were prepared by mixing 2.23 mL TEOS and 1.46 mL MTMS (or 1.46 mL DMDMS), purchased from Aldrich, at a 1:1 M ratio, and 1% europium (III) chloride (1.0 mL of the 0.1 mol L^{-1} solution) or 0.0722 g of the dipicolinate complex, which was synthesized according to the literature [33]. The ethanol was added as solvent to the mixtures, which were kept under magnetic stirring for 24 h. The gel was left to stand at room temperature for 24 h, to allow formation of the xerogel. The samples were dried at 110 °C for 1 h and ground. The final powder was washed and dried at 110 °C.

2.2. Characterization

2.2.1. Scanning electron microscopy (SEM)

The measurements were accomplished on a scanning electron microscope Hitachi TM-3000 with acceleration voltage of 15 kV. Samples in the powder form were deposited on a sample holder containing a double-faced carbon tape and were analyzed without deposition. These experiments were conducted at the Federal University of São João Del Rei, State of Minas Gerais, Brazil.

2.2.2. Thermal analysis (TG)

The thermogravimetric curves (TG) were obtained on a thermal analyzer SDT Q600 -Simultaneous DTA–TGA from TA Instruments, using a temperature gradient ranging from ambient temperature (~25 °C) to 1000 °C, at a heating rate of 20 °C/min, under a nitrogen flow of 100 mL/min.

2.2.3. X-ray diffraction (XRD)

The X-ray diffractograms were recorded at room temperature on a diffractometer Rigaku Geigerflex D/Max-c equipped with a CuKα radiation monochromator (λ=1.5405 Å). The diffractograms were registered with 2θ values ranging from 4 to 80°, at a resolution of 0.05°.

2.2.4. Photoluminescence (PL)

The excitation and emission spectra were conducted on a spectrofluorimeter SPEX fluorolog F212I equipped with a continuous xenon lamp (450 W) as the radiation source, a SPEX double monochromator model 1680, and a photomultiplier R 928 Hammatsu. The measurements were collected at 90° with respect to the incident beam. The excitation (f_{exc}) and emission (f_{em}) slits were 2.0 and 1.0 mm, respectively, which corresponded to a bandwidth of 3.40 and 1.70 nm, respectively. All the spectra were acquired at the Laboratory of Rare Earths of the Department of Chemistry of Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, University of São Paulo, Brazil.

2.2.5. Infrared spectra (IR)

The spectra of all the samples in the infrared region were achieved at the Analytical Center of the Chemistry Institute of the University of São Paulo, in São Paulo, Brazil, using the equipment Bomem model MB-102 and KBr pellets.

3. Results and discussion

3.1. Scanning electron microscopy (SEM)

The morphological characterization was carried out by SEM. Fig. 1 presents the micrographs of the samples prepared with TEOS:DMDMS or TEOS:MTMS and doped with $EuCl_3$.

The SEM images evidenced the formation of particles with distinct morphology for all the samples. Smaller particles were obtained for the sample prepared with DMDMS as compared to the materials containing MTMS. Additionally, the particles were dense and had irregular shape as well as different sizes. The type of alkoxide that was employed in the synthesis was the factor that most influenced the shape and size of the particles. Hybrids with DMDMS exhibited particles smaller than 2 μm, whereas hybrids containing MTMS were larger, with particle sizes lying between 2 and 5 μm.

Fig. 2 illustrates the SEM micrographs of the samples prepared with TEOS:DMDMS or TEOS:MTMS, doped with the europium (III) dipicolinate complex $Na_3[Eu(dpa)_3]$.

Again, the SEM images revealed the production of particles with distinct morphologies. Particles containing TEOS:MTMS were porous and displayed irregular shape as well as different sizes. The presence of much smaller particles close to the larger ones was also detected. As for the sample prepared with TEOS:DMDMS, the formation of a dense and ruffled surface with reminiscences of pores and covered with small particles was attained. This can be attributed to the presence of the $Na_3[Eu(dpa)_3]$ complex, since this was not observed in the case of hybrids prepared with $EuCl_3$. The $Na_3[Eu(dpa)_3]$ complex may have led particle growth, thereby resulting in defects on the silica surface and culminating in pores and a ruffled appearance. The hybrids had particle sizes lying around 150 and 100 μm for the samples prepared with TEOS:DMDMS and TEOS:MTMS, respectively.