Chemical Physics 511 (2018) 1–6

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Tunable excitation in Eu^{3+} based hybrid layered nanophosphors through aggregate formation

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ARTICLE INFO

Article history:
Received 30 January 2018
In final form 14 May 2018

Keywords:
Luminescence
Hybrid layered phosphors
Excitation tunability
Europium
Aggregates

ABSTRACT

A new class of Eu^{3+} based hybrid layered phosphors with tunable excitation range owing to aggregate formation is reported. The phosphors composed of layered Y_2O_3:Eu nanoparticles sensitized with 2-thenoyltrifluoroacetone (TTA) were characterized by FTIR, SEM, WAXD and photoluminescence spectroscopy. Aggregation degree between resulting hybrid layered phosphors can be successfully modulated by the solvent extraction rate and concentration when integrated into a PMMA matrix film. These films were obtained from chloroform solutions of PMMA and the layered hybrid phosphors by either drop cast or spin coating techniques on glass substrates. All the films have the characteristic "europium red" luminescence emission. The excitation spectra, on the other hand, reflects the antenna effect from the TTA ligand and, depending on the deposition technique and the phosphor concentration, the extension in the π-conjugated system (i.e. aggregation) between hybrid nanoparticles can be allowed, greatly modifying the excitation spectral characteristics.

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1. Introduction

$Y_2O_3:Eu^{3+}$ based materials are well-known red light emitting downshifting phosphors which main excitation band is associated with the O2p → Eu4f (and to higher lying Eu^{3+} ion electronic energy levels) charge transfer (CT) band at $\lambda > 250$ nm [1], leading to small optical absorption cross-section with high energy requirements. Recent research efforts have been focused in the tuning and/or broadening of the absorption band of rare earth (RE) based phosphors towards longer (more accessible) wavelengths [2–5]. One attractive approach consists in improving the luminescence of these phosphors by organic ligands attached to the phosphor particle surface through an effect known as "antenna effect" [6,7]. In this process, the organic molecule absorbs the excitation energy, which is then transferred from the ligands triplet state to the ^5D excited state of the RE ion. The antenna effect is expected to be followed by the radiative decay of the lanthanide to the ground state, emitting at a characteristic wavelength. Thanks to the organic molecule, the resulting system can provide a good optical absorption at broad UV regions which are superimposed to the resonance RE absorption peaks [8].

Layered phosphors are a new class of light emitting nanostructures and excellent candidates for the intercalation of organic sensitizers that can be exchanged while maintaining the host structure. Due to their structural anisotropy besides their interlayer chemistry with interesting behavior of swelling and exfoliation [9], the resulting layered hybrid systems have emerged as very attractive functional materials in which the host-guest interactions can be dramatically influenced by the smallest changes in the molecular conformation of the organic components. Thus, in the case of layered $Y_2O_3:Eu^{3+}$ based materials, the intercalation of organic ligands, not only would help to improve and modulate the luminescence excitation features via the antenna effect [10–12], but also these organic molecules can act as surface passivation agents, preventing surface related luminescence quenching [13], enhancing the compatibility with organic solvents and/or polymers [14].

In this work, the sensitization of layered $Y_2O_3:Eu^{3+}$nanophosphors obtained by simple solvent evaporation method [15] with TTA is reported. After TTA coordination, the hybrid layered $Y_2O_3:Eu^{3+}$/TTA nanophosphors showed an extended excitation range associated to energy transfer from TTA molecules. Finally, the hybrid nanophosphors were dispersed in PMMA/chloroform solutions and films of this composite material were deposited by drop-casting and spin-coating techniques. The effect of the hybrid

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https://doi.org/10.1016/j.chemphys.2018.05.014
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nanophosphors concentration in the PMMA matrix and of the processing conditions on the optical and luminescent properties of the films are described.

2. Experimental details

2.1. Synthesis of the layered Y_2O_3:Eu^{3+} nanophosphors (L-Y_2O_3:Eu)

The details of the synthesis of these nanophosphors can be found elsewhere [15]. They were obtained from the evaporation at 100 °C of a water solution of $Y(NO_3)_3{\cdot}6H_2O$ and $EuCl_3{\cdot}6H_2O$ followed by an annealing process at 1100 °C in an open-end hot wall tube furnace for 2 h in air.

2.2. Synthesis of the hybrid layered Y_2O_3:Eu^{3+}/TTA nanophosphors (H_xL-Y_2O_3:Eu)

0.1 g of layered Y_2O_3:Eu^{3+} was suspended in 5 mL deionized water by sonication for 5 h. Then, an appropriate amount (x) of TTA (50, 100, 300 and 500 wt% respect to L-Y_2O_3:Eu) dissolved in ethanol at 2% (w/v) concentration was added under vigorous magnetic stirring and adjusting the pH to 7 with $NaHCO_3$ which is crucial to allow the deprotonation and consequent coordination of TTA [16]. 100 mL of deionized water was added to this solution and kept at 60 °C under moderate magnetic stirring for 1 h, giving place to precipitates that were centrifuged, rinsed with ethanol and dried under vacuum at 60 °C for 24 h.

2.3. Synthesis of PMMA

20 mL of methyl methacrylate monomer (MMA) were dissolved in 80 mL of toluene, 0.048 g of benzoyl peroxide (BPO) was then added. Polymerization reaction was carried out in a 500 mL three-neck flask connected to a high purity nitrogen inlet, a condenser and a thermometer. The solution was heated at 70 °C under magnetic stirring for 10 h. The reaction mixture was then precipitated into methanol and the resulting PMMA polymer was dried under vacuum at 60 °C for 24 h.

2.4. Synthesis of the composite H_{300}L-Y_2O_3:Eu/PMMA films

PMMA was dissolved in chloroform at 1% (w/v). Appropriate amount of the H_{300}L-Y_2O_3:Eu (2, 5, 10, 20, 50 and 100 wt% respect to PMMA) was added and kept under vigorous magnetic stirring for 1 h. Three films deposited on glass substrates were obtained from each solution: drop-cast (1) and spin-coated at a spin rate of 1000 (2) and 2000 (3) rpm.

2.5. Characterization

Photoluminescence spectra were obtained using an Edinburgh Inst. M. 960 S spectrophotometer. The morphology of the powders was determined by Scanning Electron Microscopy (SEM) using a ZEISS Auriga 39–16 Electron Microscope with an accelerating voltage of 20 kV and amplification up to X5000. IR spectroscopy measurements were made in a 6700 FT-IR NICOLET. Wide-angle X-ray diffraction (WAXD) patterns were obtained using a Bruker NanoSTAR system with 1.540 Å (Cu Kα) X-ray source operating at 45 keV equipped with a Dectris PILATUS 100 K detector. Film thickness measurements were obtained on a KLA Tecnor Mod. D-600 Profiler. Optical transmittance spectra were obtained with a Perkin Elmer Lambda 25 spectrophotometer in a wavelength range of 300–1100 nm. Confocal imaging was performed at a Zeiss LSM 710 NLO laser scanning confocal microscope with a 63x oil immersion objective.

3. Results and discussion

3.1. Luminescence properties of the H_xL-Y_2O_3:Eu

Fig. 1a depicts the room temperature photoluminescence excitation spectra of L-Y_2O_3:Eu, H_{50}L-Y_2O_3:Eu (50 wt% TTA), H_{100}L-Y_2O_3:Eu (100 wt% TTA), H_{300}L-Y_2O_3:Eu (300 wt% TTA) and H_{500}L-Y_2O_3:Eu (500 wt% TTA) phosphors, monitored for the Eu^{3+} $^5D_0$-$^7F_2$ transition at 611 nm. For the L-Y_2O_3:Eu (without TTA), the excitation spectra consist of a broad band peaking at ~245 nm attributed to charge transfer (CT) from O^{2-} to Eu^{3+} ions and a shoulder at 212 nm probably associated with Y_2O_3 near band edge transitions. Upon the sensitization with TTA, two effects occur: 1) a broad band from 300 nm to 415 nm peaking at ~390 nm attributed to the direct absorption of TTA in the form of aggregates [17] appeared, evidencing the antenna effect due to the effective coordination of the ligand to the Eu^{3+} ions and b) the band from the O^{2-} to Eu^{3+} CT decreases, maybe because it competes with the TTA-Eu^3 excitation mechanism [18]. The intensity of the band at ~390 nm reached its maximum when the TTA amount (x) was 300 wt% and at this point, the CT excitation by TTA prevails over the CT from O^{2-} to Eu^{3+}. The inset in Fig. 1a shows the integrated excitation cross-section (ExCS), defined as the area under the excitation spectra in the range of 200–550 nm, as a function of the TTA content. The larger the value of the ExCS, the greater the benefit for energy harvesting of light sources emitting in this range of wavelengths [3]. It is found that, upon addition of 300 wt% TTA, the ExCS of the L-Y_2O_3:Eu is enhanced by 100%. Below 300 wt%, the amount of TTA antennas are not large enough and some Eu^{3+} ions cannot be sensitized. When the concentration of antennas is >300 wt%, a concentration quenching of the organic molecules occurs and thus luminescence intensity decreases dramatically [19].

Fig. 1b shows the photoluminescence emission spectra of L-Y_2O_3:Eu and H_{300}L-Y_2O_3:Eu measured with their corresponding peak excitation wavelengths at 245 and 390 nm, respectively. The emission spectrum from the L-Y_2O_3:Eu phosphors present a characteristic peak of the radiative transitions from the $^5D_0$ to ^7F_J (J = 0, 1, 2, 3, 4) in which the dominant peak at 611 nm corresponds to the transition from $^5D_0$ to $^7F_2$, this indicates that the Eu^{3+} ions occupy a center of asymmetry in the crystal lattice. On the other hand, when 300 wt% of TTA is added, the emission spectra of the $^5D_0$ to ^7F_J transition exhibited additional peaks at 615, 617 y 620 nm. These notable differences in the relative intensities of its five stark components could arise from the dissimilar chemical environment given by the organic ligands [20] and will be discussed in more detail in Section 3.3.

3.2. Morphology and structure of the L-Y_2O_3:Eu^{3+} and H_xL-Y_2O_3:Eu phosphors

Typical SEM images of the L-Y_2O_3:Eu and H_{300}L-Y_2O_3:Eu are shown in Fig. 2. In general, the L-Y_2O_3:Eu has a layered semi-rectangular structure (Fig. 2a) with a thickness <100 nm (Fig. 2b). After TTA-hybridization (Fig. 2c) the particle size becomes much larger because of aggregation of the H_{300}L-Y_2O_3:Eu layers, facilitated by the organic ligand at their surfaces, which in turn explains the extended excitation spectra features. Nevertheless, the H_{300}L-Y_2O_3:Eu maintains the laminar morphology and can always be easily re-dispersed in common organic solvents. It is worth mentioning that this improved compatibility with common organic solvents is highly desirable for any application that could require processing in the solution phase with high homogeneity and transparency requirements (See support information Fig. S1).

FTIR spectra, taken for the H_{300}L-Y_2O_3:Eu and compared with those from the pure TTA and L-Y_2O_3:Eu (Fig. 3), corroborate the

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