
Sol-gel derived Luminescent Coatings Incorporating YVO₄:Eu³⁺ Nanocrystals for Narrow-Red Emission

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Abstract

- Introduction

In recent years, the emergence of luminescent coatings with exceptional quantum yield has marked a pivotal advancement in the pursuit of miniaturizing optical systems like LED lighting and display devices (1). Herein, we have studied the influence of NPs size on the optical properties of luminescent coatings. To this end, two types of YVO₄:Eu³⁺ NPs, with average diameters of 10 nm and 340 nm, were synthesized by two different hydrothermal processes (2,3). This lanthanide ions doped vanadate is well-known to produce a strong narrow red emission upon UV excitation. Furthermore, an inorganic-organic hybrid material was developed using the sol-gel synthesis method. The precursor sol was prepared through the hydrolysis and condensation of 3-glycidoxypropyltrimethoxysilane (GPTMS) combined with zirconium propoxide, which was chemically stabilized using acetylacetone as a complexing agent. Afterwards, these YVO₄:Eu³⁺ NPs were incorporated in this hybrid material with different loading rates and then luminescent coatings were achieved by spin-coating these suspensions onto glass substrates. Finally, the angular emission distribution was analyzed to estimate the photons trapped inside the structure depending on the surface roughness and the NPs size.

PACS Keywords: YVO₄:Eu³⁺ nanoparticles, hydrothermal synthesis, hybrid material, sol-gel, luminescent coatings

- 2. EXPERIMENTAL SECTION

2.1. Synthesis of YVO₄:Eu³⁺ Nanoparticles

Eu-doped YVO₄ nanoparticles were synthesized by two different hydrothermal protocol. In the first synthesis (S1-synthesis), a solution containing Y, Eu, and citrate was mixed with NaVO at pH 13 and aged at 90°C. The mixture was then hydrothermally treated at 180°C for 15 hours, followed by centrifugation, washing, and drying to obtain the final product (S1-nanoparticles) (2). In the second synthesis (S2-synthesis), Y and Eu precursors were

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hydrothermally treated at 200°C for 1 hour. The product was purified using etidronic acid under acidic conditions, followed by alkalization, centrifugation, washing, and drying (S2-nanoparticles) (3). Various doping concentrations of 0% (undoped), 5% and 15% by using two different synthesis protocol.

2.2. Synthesis of hybrid material

Hybrid material was synthesized using sol-gel method.

3-Glycidyloxypropyltrimethoxysilane was hydrolyzed in ethanol with hydrochloric acid to form sol 1. Separately, zirconium tetra-n-propoxide was stabilized with acetylacetone in ethanol and added to sol 1, stirred overnight to obtain sol 2, which was stored at 5°C (4).

• 3. RESULTS AND DISCUSSION

3.1. Characterization of S1- and S2-Nanocrystals

The synthesized S1 and S2-YVO₄:Eu³⁺ nanoparticles were structurally and morphologically characterized using XRD, Raman, FTIR analyses and TEM analysis. Eu³⁺ concentration was evidenced by elementary analysis and Rietveld refinement. The average diameter of the S1 and S2 nanoparticles were calculated to be 340 nm and 10 nm (**Figure 1**).

Figure 1. (A) TEM Images of S1 and S2-YVO₄:Eu³⁺ NCs.

The emission spectra are dominated by strong 5D₀-7F_{2,4} electric-dipole transitions at 619 nm and 698 nm, respectively, intensified by the D_{2d} site symmetry of Eu³⁺ (**Figure 2**). Weaker 5D₀-7F_{1,3} magnetic-dipole transitions also appear. In the excitation spectra, a broad absorption band appears between 250 and 375 nm in the narrow band UVB range, corresponding to charge transfer excitation from the oxygen ligands to the central vanadium atom in the VO₄³⁻ groups (5).

Figure 2. Emission spectra of S1- and S2- nanocrystals

Quantum yield studies were conducted to assess the efficiency of the synthesized nanocrystals (NCs). The external photoluminescence quantum yield (ePLQY) of S1-YVO₄:Eu³⁺ (5 %) and S2-YVO₄:Eu³⁺ (5 %) NCs were 27.2% and 43.9%, respectively. Interestingly, the smaller S2 NCs showed higher ePLQY, aligning with decay data. This improvement is likely due to better crystallinity and lesser surface defects, even without thermal treatment.

3.2. Characterization of luminescent coatings

The preparation of the hybrid material through a sol-gel process and the subsequent fabrication of luminescent coatings are realized with loading concentration of 2 wt.% and 5 wt.% in YVO₄:Eu³⁺ NCs (**Figure 3**). The process ensures uniform distribution of nanocrystals within the hybrid matrix. Their thickness was determined by profilometry and micro-reflectivity measurements. Furthermore, the effect of mass loading and nanoparticle size on the optical properties of luminescent films was also investigated by conducting photoluminescence and UV-visible spectroscopies. Coatings exhibit bright red emission, confirming effective incorporation of YVO₄:Eu³⁺ NCs. Homogeneity of luminescent coatings assessed using a video colorimeter.

Day light

$\lambda_{\text{exc}} = 254 \text{ nm}$

Figure 3. (A) Image of prepared transparent hybrid material coating and (B) Image of nanophosphor encapsulated coating.

• 4. CONCLUSION

In this study, we developed and characterized luminescent coatings by embedding YVO:Eu³ nanocrystals into a hybrid sol-gel matrix. We examined how variations in nanocrystal size and synthesis conditions influence their optical properties, aiming to optimize performance for potential photonic applications. The study concludes with insights into the trade-offs between transparency, quantum yield, and luminescence intensity in luminescent coatings. Future research aims to enhance photon scattering and reduce losses through innovative strategies. Smaller nanoparticles (S2) show higher ePLQY due to improved crystallinity and ligand protection. Larger nanocrystals (S1) exhibit reduced photon leakage and higher luminescence intensity. Future strategies include integrating metallic nanoparticles to enhance photon scattering and minimize guiding losses.

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