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SiO_2@LaOF:Eu^{3+} core-shell functional nanomaterials for sensitive visualization of latent fingerprints and WLED applications

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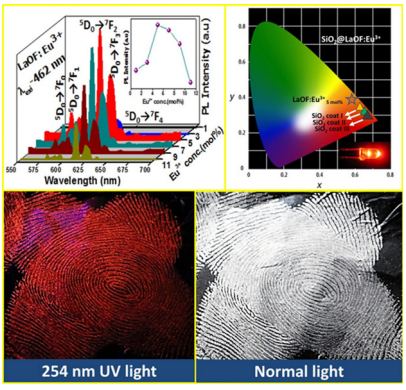
HIGHLIGHTS

- Solvothermal route is employed to fabricate nanostructured core–shell SiO_2@LaOF:Eu^{3+}.
- Core-shell and the number of coats were confirmed using advanced techniques.
- Luminescence quantum efficacy of 56.7% was observed for the prepared samples.
- Latent finger prints up to level-3 were recognized by using these powders as dust.
- Forensic and security applications were realized with the prepared samples.

GRAPHICAL ABSTRACT



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ABSTRACT

For the first time, intense red color composite of SiO_2@LaOF:Eu^{3+} core-shell nanostructures (NS) were fabricated via facile solvothermal method followed by thermal treatment. The obtained core–shell particles display better spherical shape and non-agglomeration with a narrow size distribution. Photoluminescence (PL) emission spectra exhibits intense peaks at ~593 nm, 611 nm, 650 nm corresponds to $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1 and 2) Eu^{3+} transitions respectively. The spectral intensity parameters and Eu-O ligand behaviors are estimated by means of Judd-Ofelt (J-O) theory. CIE co-ordinates are found to be (x = 0.63, y = 0.36) which is very close to standard NTSC values (x = 0.67, y = 0.33). CCT value is ~3475 K which is less than 5000 K, as a result this phosphor is suitable for warm light emitting diodes. The optimized core-shell SiO_2 (coat III)@LaOF:Eu^{3+} (5 mol%) was used as a fluorescent labeling marker for the visualization of latent fingerprints on both porous and non-porous surfaces. Obtained fingerprints are highly sensitive and selective also no background hindrance which enables level-I to level-III fingerprint ridge characteristics. Observed results indicate that the significant improvement in luminescence of coreshell NS can be explored as a sensitive functional nanopowder for advanced forensic and solid state lightning applications.

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1. Introduction

In recent years, core–shell structures have attracted extensive scientific and technological interests owing to its fine-tuning of the properties. A large number of hard and soft templates, are used to fabricate various composite structures. Among the diverse templates, silica is regularly used in core-shell structured materials, owing to its tunable sizes [1–4]. When nanoparticles are used as shells are coated on the silica cores, a type of core–shell phosphor with spherical morphology is obtained. Further, by tuning the experimental conditions and method of fabrication, non-agglomerated, perfect spherical shaped particles can be prepared. This helps to achieve least scattering of light with improved brightness as well as good resolution. These properties are useful for display devices, bio-medical imaging and anti-counterfeiting applications [5–12].

The luminescent properties of rare earth (RE) doped nanophosphors have special properties such as sharp absorption and emission lines in UV–Vis region with high quantum yield, long lifetime and higher photostability, good thermal & chemical stability, excellent biocompatibility and non-toxicity. Quantum efficiencies for recently reported oxide hosts are: For $Sr_4Al_{14}O_{25}$ – 38% [13]; $Ca1_4Al_{10}Zn_6O_{35}$ – 50% [14]; $CaAl_{12}O_{19}$ – 35.5% [15]; $Sr_4Al_{14}O_{25}$:Mn^{4+}, Na^+, B^{3+} – 60.8% under 450 nm blue light excitation [16]; $CdGdAlO_4$: Pr^{3+}, Yb^{3+} – 166% [17]. Further, due to their similar ionic radii, trivalent luminescent lanthanide (Ln^{3+}) ions can easily be integrated into the crystal structure of fluoride based host matrices and display highly efficient luminescence even at room temperature [18–21].

Among the various RE ions, Eu^{3+} ion is the best dopant for many hosts for producing red color emission which is considered as a long photoluminescence lifetime of the order of several milliseconds or longer [22]. Till date a variety of host matrices have been used for doping of luminescent Eu^{3+} ions namely oxides, phosphates, vanadate, molybdates, borates and fluorides. Among these hosts, rare-earth fluorides are found to be exceptionally stable hosts for doping of several optical active Ln^{3+} ions. These materials have high refractive index, low phonon energy, high ionicity, good resistivity and ionic conductivity, which lead to the low possibility of non-radiative decay and subsequently the luminescence quantum yield is greater in these hosts [23]. The surface modification is found to be one of the most capable as well as effective methods which changes the distance between luminescent and quenching centers lowers the surface defects and reduces the non-radiative channels. Because of all these consequences, luminescent improvement can be attained in a coreshell nanostructure [8,24].

Recently, RE doped nanomaterials with less than 100 nm have recognized much attention in surface based research especially in latent fingerprints (LFPs) recognition [25–27]. Conversely, the levels of visualization are not well recognized due to the poor fluorescent image abilities with these nanomaterials. Thus, it is critical to develop a simple, cost-effective, non-destructive, precise method for stress-free visualization of LFPs fluorescent powders of nontoxic, highly chemical/thermal stability high contrast, high selectivity, low background interference, and high-efficiency in nature [28–33].

Due to the limitations of current imaging technologies and instruments, recognition of LFPs is mostly based on the level II structures (such as ridge termination, bifurcation, and crossover), which is the basis of the universal recognition. To guarantee the accuracy of identification, the needed number of the level II characteristics set must vary from 6 to 17. However, the distribution of the level II structures on fingertips is arbitrary, so it needs relative large fingerprint images to achieve accurate fingerprint identification. In real situations, the collected LFPs may be sometimes incomplete, and even don't have enough characteristics features. Therefore, more characteristics other than level II of fingerprints are needed for better recognition. Besides level II structures, the level III characteristics (sweat pore) on fingertips are also permanent, immutable and unique, which may help the fingerprint analysis more effectively [34,35].

In the present study, optimized core-shell composite of SiO_2@-LaOF:Eu^{3+} phosphors are used as unique fluorescent label for the visualization of level I to level III ridge patterns on various surfaces. Various characterization and optical properties were studied the prepared samples. Further, anti-counterfeiting and forensic applications are studied in detail.

2. Experimental

2.1. Materials

The chemicals used in the present work are Lanthanum(III) nitrate hexahydrate [$La(NO_3)_3{\cdot}6H_2O$ (Sigma Aldrich; 99.9%)], Ammonium fluoride [NH_4F; (Sigma Aldrich; 99.9%)], Europium (III) nitrate pentahydrate [$Eu(NO_3)_3{\cdot}5H_2O$; (Sigma Aldrich; 99.9%)], Tetraethyl Orthosilicate [$Si(OC_2H_5)_4$:10.41 mL], Poly Ethylene Glycol (PEG) [$H(OCH_2CH_2)_nOH$], Thiourea ($SC(NH_2)_2$), Polyvinylpyrrolidone [$(C_6H_9NO)n$].

2.2. Preparation of core SiO_2 and core–shell SiO_2@LaOF:Eu^{3+} (5 mol%) NS

Mono disperse SiO_2 micro spheres are synthesized by the well-known Stöber method [36]. In a typical preparation process, Eu^{3+} doped LaOF NS are coated onto the as-prepared silica cores by a solvothermal method. In the first stage, 1 g of prepared silica spheres is dispersed in 60 mL of PEG and 1.95 mL of $La(NO_3)_3{\cdot}6H_2O$ (1.0 M), NH_4F(1.0 M) and 1 mL of $Eu(NO_3)_3{\cdot}5H_2O$ (0.05 M) are added into the above mixture under constant stirring. Then, 1.5 g of Polyvinylpyrrolidone (PVP K30, M = 40,000) is dissolved in the mixture thoroughly. Afterwards, 10 mL of ethanol solution containing 0.11 g of Thiourea ($SC(NH_2)_2$) is added drop wise into the above solution with vigorous agitation. Further, 1 mL of NaOH solution (2 M) is gradually added to the mixture as a precipitating agent. After being stirred for another 1 h, the mixture is transferred to a 150 mL Teflon-lined autoclave and heated at 180 °C for 36 h. When the autoclave is cooled to RT, the precursors are separated, washed and dried at 60 °C followed by calcined at 800 °C for 2 h. The step by step formation process of core-shell SiO_2@LaOF:Eu^{3+} (5 mol%) NS is shown in Fig. 1.

2.3. Visualization of LFPs and security ink by using core–shell SiO_2@LaOF:Eu^{3+} (5 mol%) NS

The LFPs visualization is carried out via a typical powder dusting method using optimized core–shell SiO_2@LaOF:Eu^{3+} (5 mol%) NS as fluorescent labeling marker. The detailed experimental procedure for the visualization of LFPs on various porous and non-porous surfaces is described elsewhere [37]. The optimized SiO_2 (coat III)@LaOF:Eu^{3+} NS is well dissolved in a PVC gold medium using ultrasonication to achieve security ink with the most favorable performance, such as viscosity and surface tension. The resultant solution is used as a dip pen security ink and photographed under UV excitation (254 nm wavelength).

3. Characterization

Shimadzu X-ray diffractometer (PXRD-7000) using Cu Kα radiation (λ = 1.541 Å) is used to study the crystalline purity and phase