Research Article

Stress-Induced Structural Phase Transition in Polystyrene/NaYF₄: Eu³⁺ Photoluminescent Electrospun Nanofibers

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Polystyrene (PS) composite nanofibers were successfully fabricated by embedding NaYF₄: Eu³⁺ nanophosphor into the PS matrix via electrospinning. The photoluminescence spectra, surface morphology and crystal structure of nanofibers were characterized by photoluminescence spectroscopy, scanning electron microscopy, and X-ray diffractometer, respectively. Stress-induced α-NaYF₄: Eu³⁺ (cubic) to β-NaYF₄: Eu³⁺ (hexagonal) structural phase transformation was observed in the nanofibers. The stress-induced phase transformation provides enough space for tailoring the properties of novel nanostructures. The composite nanofibers exhibited blue emission with 239 nm excitation wavelength. The XRD pattern of espun nanofibers confirmed the successful incorporation of 5% NaYF₄: Eu³⁺ nanophosphors into the PS matrix. Brilliant values of the chromaticity coordinates of the prepared photoluminescent nanofibers (PLNs) predict their possible use in blue solid-state lighting applications.

1. Introduction

The twenty-first century is enriched by various nanostructures and nanomaterials such as nanotubes, nanofibers, nanoribbons, nanowires, nanocubes, and nanobelts. One-dimensional (1-D) nanofibers have gained significant attention in the research community due to their unique and extraordinary properties among the various nanostructures. Nanofibers have a diameter of less than 100 nm with very high porosity. The high surface area to volume ratio makes them unique for diverse applications such as optoelectronics, biomedical engineering, luminescent fabrics, solar sensors, food packaging, and nanotechnology [1–4]. Among many available techniques, electrospinning is popular in producing long, continuous, fine fibers of variable diameter [5]. In addition to compatible solvent with polymer, some quantity of surface tension solvents or a small amount of pyridine/ionic salts into the solution helps to obtain nanofibers with a small diameter [6].

In recent years, the fabrication of polyacrylonitrile (PAN), polyethylene oxide (PEO), poly (methyl methacrylate) (PMMA), polyvinylidene difluoride (PVdF), poly (vinyl alcohol) (PVA), poly (vinyl pyrrolidone) (PVP), and PS electrospun polymeric light-emitting nanofibers has been studied with different functional additives [7–11]. Herein, polystyrene is considered for the preparation of nonbiodegradable photoluminescent nanofibers using the electrospinning technique. Polystyrene is composed of a long chain of a hydrocarbon having excellent properties such as stiffness, surface quality, and transparency. Therefore,
polystyrene is being utilized in different areas of research. Generally, PS is inert which does not show emission in the visible region [12, 13].

Recently, it can be seen that upconversion nanophosphors (UNCPs) are playing a vital role in biosensing, bioimaging, and solid-state lighting applications. UNCPs are nanoparticles, nanocrystals and microcrystals of lanthanide-doped rare earth fluorides [14, 15]. Several studies have been reported on Eu-doped phosphors with different hosts such as Sr₂In-TaO₆, Lu₂O₃, GdOF, NaYF₄, and (TTA)₃phen for solid state lightening applications [16–22]. Eu³⁺ ions show outstanding luminescent properties among lanthanides. Sodium yttrium fluoride (NaYF₄) is a wonderful up or down conversion host lattice. NaYF₄ leads to intensify the luminescent properties significantly. NaYF₄ nanophosphors show a phase transformation in the structure from α-NaYF₄ (cubic) to β-NaYF₄ (hexagonal) by changing external parameters like temperature and fabrication process. The lanthanide-doped hexagonal phase of NaYF₄ nanocrystals exhibits marvelous luminescence properties because of its low phonon energy [23–26].

Residual stress is one of the important mechanical signatures of atomic and molecular scale in a nonequilibrium state. The stress is generally occurred in the materials by the action of external fields, which is an ambient outcome of solid materials processing at the nanoscale. It remains in the materials even after the removal of applied forces. Usually, as materials are processed for the development of new structures, they are influenced by the nonequilibrium state [27]. The stress performs a significant role in tailoring the performance and reliability of the nanostructures. During the fast fabrication processes, the stress is directly related to the macromolecule chain locking of polymer matrices [28]. The polymeric products demonstrate the stress during the synthesis of thin films, fibers and devices at the nanoscale. Molecular weight, elastic stiffness and glass transition temperature of polymer matrix are the important factors that are contributing to the stress-like phenomena. Therefore, stress is passed on from the polymer matrix to the embedded nanoparticles by the interfacial shear during the synthesis processes [29, 30].

Few research studies have been reported on the photoluminescence properties of PS electrospun nanofibers using inorganic and organic nanoparticles as functional additives. Inorganic nanoparticles incorporating PS composite electrospun nanofibers revealed photoluminescence emission characteristics peaks from 510 to 615 nm, whereas emission peaks were observed from 532 to 612 nm for the organic additive-based PS nanofibers [31–33]. In the present article, facile fabrication of PS composite nanofibers using the electrospinning technique is reported. A phase transformation of NaYF₄ from cubic (Fm3m) to hexagonal (P6₃/mmc) has been observed for polymeric electrospun nanofibers. PS polymer was used as a novel material for incorporating and aligning the synthesized phosphor material in nanofiber morphology. So, the novelty of the material lies in the novel precursor nanofibers fabricated incorporating the Eu³⁺ doped NaYF₄ material and observation of phase change in the synthesized material after incorporation. The study will give insight to the readers about the new electrospinning technique for PLNs fabrication with occurred changes in material via stress induced during electrospinning. The characteristic emission peak is observed at 612 nm, which is possibly efficient for illuminating the solid-state lighting applications.

2. Materials and Methods

2.1. Materials. All required materials of 99.9% purity were obtained from Thomas Baker Chemicals Pvt. Ltd., Mumbai, India, for the preparation of the nanophosphor. The reagents have been utilized without any purification in the
2.2. Methods: Electrospinning. Nanofibers were fabricated using an electrospinning machine, ESPIN-NANO PICO, Chennai. 25 mg of nanophosphors was added in 4.6 gm of DMF solution. Immediately, ultrasonication of the solution has been done for 45 minutes at 40°C temperature. Furthermore, 500 mg of polystyrene was poured into the same solution and sonicated for 90 minutes. In addition, a 12-hour vigorous magnetic stirring was given to the polymeric solution and sonicated for 90 minutes. In addition, a 12-hour vigorous magnetic stirring was given to the polymeric solution and sonicated for 90 minutes. Experimentally, 500 mg of polystyrene was added in a syringe having 24 nozzle gauges of a needle for electrospinning.

Figure 1 shows the schematic design of the electrospinning process for the preparation of PS/NaYF₄: Eu³⁺ PLNs. Needle tip to collector distance was kept between 20 cm and 18 kv, and DC voltage was applied between them. The diameter and shape of the nanofibers were controlled by applying high potential. As the potential increases up to the critical limit [35], the flow rate of the solution and the speed of the collector were kept at 0.3 ml/h and 2000 rpm, respectively. Espun nanofibers were collected on aluminum sheets of size 14 cm × 13 cm having 0.158 mm thickness.

3. Results and Discussion

3.1. X-Ray Diffraction. X-ray diffraction pattern of PS composite nanofibers was taken by Rigaku Japan X-ray diffractometer having Cu-Kα radiation with a wavelength of λ = 0.15406 nm in the 2θ range of 10-80°. Figure 2 demonstrates the X-ray diffractions of PS composite nanofibers. The peak centered at 2θ = 19° (green triangle) is assigned for PS. The aluminum (Al) foil peaks are 38.57°, 44.75°, 65.32°, and 78.48° (violet pentagon). The blue circled peaks 28.22°, 42.02°, 58.22°, 69.53°, and 78.25° (blue circle) correspond to α-NaYF₄ (Cubic, JCPDS No. 77-2042) (Fm3m) are associated to crystal planes (111), (220), (222), (400), and (420), respectively. While the red squared peaks at 19.88°, 29.03°, 34.88°, 38.46°, 43.31°, and 72.44° (red square) corresponding to β-NaYF₄ (hexagonal, JCPDS No. 28-1192, P6₃/mmc) are associated to crystal planes (111), (110), (200), (111), (201) and (311), respectively.

When the α-NaYF₄ parent cubic phase is subjected to external stress, it shows the transition into the β-NaYF₄ daughter hexagonal phase, which has lower energy than the parent phase. The cubic and hexagonal phases are present in the PS/NaYF₄: Eu³⁺ nanofibers. This phase transition occurs because of the stress being transferred from the PS polymer to the embedded unit cells of nanophosphors within the fibers. The diffraction peaks of α-NaYF₄: Eu³⁺ are attributed to pure cubic NaYF₄, whereas XRD peaks of β-NaYF₄: Eu³⁺ are assigned to hexagonal NaYF₄ (Figure 2). When Eu³⁺ ions are dispersed with such disordered crystal, the coordination environment of Y³⁺, around the ions will deform the lattice. It happens due to the mismatch of ionic radius of Y³⁺ (0.89 Å) and Eu³⁺ (0.95 Å). A left shift of the X-ray peak juxtaposed with the peak of a single crystal reveals a decrease in d-spacing. It means the tensile stress acting on the crystal structure and vice versa an increase in d-spacing is the signature of compressive stress. Then, the stress is calculated by the multiplication of the average strain and elastic constant of the nanofiber. As strain is fundamental, in this study, PS composite nanofiber concerning strain is characterized [36–38].

Figure 3 indicates the phase transition in the NaYF₄ crystal structure. The visualization for electronic and structure analysis (VESTA) tool has been used to visualize the structure [39]. The applied tensile stress minimizes the energy barrier for α to β phase transition, while it maximizes the energy barrier for the reverse transition from the β phase back to the α phase may occur. Shear deformation is the principal operation of the slip system. The effective stress can be large enough to overcome the energy barrier or
Burger’s vector and exceeds the critical shear stress required to activate the lattice plane slide/slip \[40, 41\].

Typically, polymer structures consist of both amorphous and crystalline linear molecular chains. The properties of the polymer matrices are dependent upon the arrangement of the molecules in structure. The polymeric structure is said to be crystalline if the alignment of the linear molecules is systematic, whereas the unsystematic arrangement of the molecules approaches to amorphous structures. The crystalline polymers can be understood by the well-known folded chain theory for polymeric structures. The beauty of crystalline polymer matrices is that they are brittle in nature which leads them to better optical properties. It is also to be noted here that higher crystalline polymer matrices have a high refractive index, which makes them translucent in nature, while the amorphous polymer matrices show their transparent nature entirely \[42\]. Table 1 shows the refractive indices of a few polymer matrices.

Kumar et al. have incorporated the NaYF\(_4\):Eu\(^{3+}\) nano-phosphors into the PVA \[34\], PAN \[47\], and PMMA \[48\] matrices using electrospinning. However, stress-induced phase transition didn’t find in electrospun nanofibers with the phosphor nanoparticles Zare et al. observed that the stress is transferred from the polymer matrix to embedded nanoparticles in a polymeric nanocomposite. An imperfect interface like a polymer cannot bear the large interfacial shear stress. Such deformation minimizes the interfacial shear stress that initiates a slower transfer of normal stress in platelets/nanoparticles \[49–51\]. When a polymer is crystalline enough, it transfers the maximum stress to the embedded nanoparticles resulting in the stress-induced phase transition which is observed in polymeric nanocomposites and nanofibers. The PS polymer is more crystalline than PVA, PMMA and PAN matrices, which enables PS to transfer the shear stress to the nanophosphor. The hexagonal phase of \(\beta\)-NaYF\(_4\) UNCPs is more stable than \(\alpha\)-NaYF\(_4\) which has been observed in PS/NaYF\(_4\): Eu\(^{3+}\) PLNs via phase transformation. The PS nanofibers get stressed during the electrospinning process. Hence, they transferred the stress to the cubic unit cell, resulting in the hexagonal phase of the nanophosphor being obtained. The strain is calculated for (111) and (222) planes 0.000521 and 0.002741, respectively. This amount of strain is enough to activate the slip/slide (111) plane of \(\alpha\)-NaYF\(_4\) to the basal slip plane (0001) of the \(\beta\)-NaYF\(_4\) phase.

The cubic structure of NaYF\(_4\) has been confirmed by XRD with the lattice parameters (cal) of \(a=b=c=5.48\) Å along with the angles \(\alpha=\beta=\gamma=90^\circ\), whereas the hexagonal structure affirmed with the lattice parameters of \(a=b=5.96\) Å, \(c=3.53\) Å, \(\alpha=\beta=90^\circ\) and \(\gamma=120^\circ\). The crystal size of \(\alpha\) and \(\beta\) crystals has a diameter of 46.18 nm and 70.25 nm in PS nanofiber, respectively. \[52\]

3.2. Surface Morphology. ZEISS EVO 18 scanning electron microscopy (SEM) has been used to investigate the morphology of the electrospun nanofibers. Figures 4(a)–4(d) show the SEM micrographs of randomly aligned PS/NaYF\(_4\): Eu\(^{3+}\) nanofibers with different flow rates 0.1, 0.15, 0.2 and 0.3 ml/h, respectively, at 5%. The flow rates 0.1, 0.15, 0.2 and 0.3 ml/h are optimized during the electrospinning process and found that 0.3 ml/h flow rate is appropriate for the good surface morphology of spun nanofibers. Not only the concentration but the flow rate of PS solution has also
Figure 5: Continued.
Figure 5: Texture analysis of PS nanofibers: (a–d) show the fiber diameter distribution (FDD) at 0.1, 0.15, 0.2 and 0.3 ml/h flow rate and (e–h) show the bead size distribution (BSD) @ 0.1, 0.15, 0.2, and 0.3 ml/h flow rate.

Figure 6: (a) Photoluminescence (PL) spectra of PS composite nanofibers at 5%, (b) chromaticity (CIE-1931) emission coordinates (X = 0.17, Y = 0.07) extracted from the PL spectra of nanofibers corresponding to 239 nm excitation wavelength, and (c) charge transfer (CT) band in comparison with f-f transitions bands.
Table 2: Experimental Judd-Ofelt intensity parameters, radiative emission rates ($A_{\text{rad}}$), nonradiative decay rates ($A_{\text{nrad}}$), intensity ratio, parameter sum efficiency of PS/NaYF$_4$: Eu$^{3+}$ nanofibers.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Judd-Ofelt intensity parameters ($X 10^{-20} \text{cm}^2$)</th>
<th>Radiative emission rates ($A_{\text{rad}}$) (s$^{-1}$)</th>
<th>Nonradiative decay rates ($A_{\text{nrad}}$) (s$^{-1}$)</th>
<th>Intensity ratio ($I_2/I_1$)</th>
<th>Quantum efficiency $\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/NaYF$_4$: Eu$^{3+}$</td>
<td>$\Omega_2$ = 5.05, $\Omega_4$ = 0.40</td>
<td>230.58</td>
<td>7521.35</td>
<td>2.92</td>
<td>2.97</td>
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influenced the morphology of electrospun nanofibers. SEM pictures reveal that beads are present in the nanofibers which are prepared by following the flow rates 0.1, 0.15 and 0.2 ml/h. As the flow rates of the PS solution are increased from 0.1 to 0.3 ml/h, the nanofibers become uniform, and their beads almost vanished. Therefore, the flow rate plays a vital role in the electrospinning process. Generally, an accurate flow rate improves the surface morphology of electrospun nanofibers.

The texture analysis of PS composite nanofibers is shown in Figure 5. The diameter of nanofibers and their bead component analysis is shown in the histogram studied by ImageJ software. The average diameter of nanofibers is found 354 nm, 351 nm, 297 nm and 361 nm at 0.1, 0.15, 0.2 and 0.3 ml/h flow rate, respectively, whereas the bead components have the diameter as 1.8 mm, 1.16 mm, 1.10 mm and 451 nm for the same flow rates.

It is concluded from the histogram from e to h that the number of bead components decreases as the flow rate increases. The obtained nanofiber mat consists of the network-like structure at 5% concentration of nanophosphor in the PS matrix at 0.3 ml/h flow rate with an average diameter of 350 nm.

3.3. Photoluminescence (PL) Spectra. The PL spectra of PS were recorded at 239 nm excitation wavelength using the spectrometer Perkin-Elmer LS 55. The photoluminescence spectra of PS composite beaded nanofibers are shown in Figure 6(a) with an emission peak in the inset. PS composite nanofibers exhibit emission intense peaks at around 590 nm and 612 nm with 239 nm excitation wavelength. The characteristic emission lines shown in the inset are associated with the Eu\(^{3+}\) transitions from the excited \(^5\)D\(_{0}\) \(\rightarrow\) \(^7\)F\(_{J}\) level, a transition of Eu\(^{3+}\), where \(J\) ranges from 0 to 2, that is, 590 nm, \(^5\)D\(_{0}\) \(\rightarrow\) \(^7\)F\(_{1}\); 612 nm, \(^5\)D\(_{0}\) \(\rightarrow\) \(^7\)F\(_{2}\). The International Commission on Illumination (CIE) 1931 has been utilized to understand the color quality from composite nanofibers.

The color space chromaticity diagram of PS composite nanofibers is shown in Figure 6(b) at 239 nm with the color coordinates of \(X = 0.17\) and \(Y = 0.07\). The luminescence of Eu\(^{3+}\) ions attributes to the phenomenon of excitation which is due to charge transfer (CT), enhancing the emission effectiveness. Figure 6(c) shows that a charge transfer (CT) band is significantly wider and much more intensive in comparison with f-f transitions bands. The nonradiative recombination of the excitons can be controlled through the charge or energy transfer process during the fluorescence quenching. Therefore, NaYF\(_{4}\) emission will not be affected or slightly changed, and hence, the tunability can be achieved.

The Judd-Ofelt intensity parameters were determined using LUMPAC package [53, 54]. All the calculated quantities (\(\Omega_2, \Omega_4, A_{\text{rad}}, A_{\text{int}}, I_{2}/I_{1}\), and \(\eta\)) are shown in Table 2.

4. Conclusions

In conclusion, PS composite nanofibers are fabricated using an electrospinning technique having an average diameter of 361 nm. The morphology of PLNs reveals that an optimum flow rate is required for the preparation of uniform electrospun nanofibers. The bead components lost their identity properly with varying flow rates from 0.1 to 0.3 ml/h. XRD results not only confirmed the phase transition from cubic to hexagonal but also a homogeneous dispersion of NaYF\(_{4}\); Eu\(^{3+}\) nanophosphors into the PS matrix. The hexagonal phase is achieved due to the shear stress exerted on the nanofiber. The typical emission transition \(^5\)D\(_{0}\) \(\rightarrow\) \(^7\)F\(_{2}\) exhibits the chemical environment of Eu\(^{3+}\) ions. These results demonstrate the possible use of PS espun composite nanofibners in solid-state lighting, biosensing and bioimaging applications. The concentration of the nanophosphors into the PS matrix is also an important factor for affecting the PL properties during electrospinning. By varying the concentration of the nanophosphors in the PS matrix, the PL properties of espun nanofibers can be enhanced in future studies. Future studies will focus on the potential use of PS espun nanofibers in flexible lightening applications.

Data Availability

The data used to support the findings of this study are included within the article. Should further data or information be required, these are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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