Tunable Photoluminescence of Polyvinyl Alcohol Electrospun Nanofibers by Doping of NaYF₄: Eu⁺³ Nanophosphor

Sanjeev Kumar, Garima Jain, B. P. Singh, and S. R. Dhakate

1Department of Physics, R K (PG) College Shamli, UP, India
2Department of Physics, D A V (PG) College Muzaffarnagar, UP, India
3Advanced Carbon Products and Metrology Section, Advanced Materials and Devices Metrology Division, CSIR-National Physical Laboratory, 110012, New Delhi, India

Correspondence should be addressed to Sanjeev Kumar; sanjeev.raonpl@gmail.com

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NaYF₄: Eu⁺³ nanophosphor/polyvinyl alcohol (PVA) composite nanofibers have been successfully fabricated using the electrospinning technique. The electrospun polymeric nanofibers were characterized by scanning electron microscopy (SEM), high-resolution transmission microscopy (HRTEM), X-ray diffraction (XRD), photoluminescence (PL), and Raman spectroscopy. The flexible polymeric mats exhibited strong red emission at 724 nm at excitation wavelength of 239 nm. 5% concentration of NaYF₄: Eu⁺³ nanophosphor are embedded homogenously inside the PVA matrix. The strong red emission peak attributed to the presence of Eu⁺³ ions. The characterization of the mats confirmed the uniform dispersion and tunable photoluminescence properties. These photoluminescent nanofibers (PLNs) could be easily fabricated and potentially useful in solid-state lighting applications.

1. Introduction

The fascinating one-dimensional (1D) nanostructures have captured the attention of scientific community because of their outstanding properties such as high surface area to volume ratio and flexible and tunable surface morphologies. The 1D nanofibers have already been prepared by catalytic synthesis, interfacial polymerization, vapor deposition, vapor-phase transport process, gel spinning, electrospinning, self-assembly, template synthesis, melt spinning, electrostatic spinning and drawing, etc. [1–4]. But the electrospinning technique is the best choice for nanofiber fabricators because of its versatile properties. There is no doubt that this technique is cost-effective, simple, and convenient that utilizes electrostatic forces to fabricate polymeric exceptionally long and uniform 1D nanofibers with large surface area and high length-diameter ratio [5–8]. It is successfully developing continuous and long ultrathin fibers from polymers, composites of inorganic and organic luminescent nanoparticles with polymers, metals, and semiconductors, with diameters ranging from micrometer (μm) to nanometer (nm). In most of the studies, electrospun nanofibers have been prepared for the solid-state lighting from various polymers such as polyvinyl alcohol (PVA), polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(ethylene oxide) (PEO), polyvinylpyrrolidone (PVP), polyvinylidene difluoride (PVdF), polyvinylcarbazole (PVK), poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV), and polydiallyldimethylammonium chloride (PDAC) by using different additives. These polymers are being used to fabricate the light-emitting nanofibers via the electrospinning technique. Cadmium sulfide (CdS), cerium-doped yttrium aluminum garnet (YAG: Ce³⁺; Y₃-xAl₅ O₁₂: Ceₓ³⁺), silica nanoparticle (SNP), fullerene (C₆₀), europium-doped lutetium oxide (Lu₂O₃:Eu³⁺), europium-doped zirconium dioxide (ZrO₂:Eu³⁺), germanium nanocrystals (Ge-NCs), terbium-doped silicon dioxide (SiO₂: Tb³⁺), europium, ytterbium, erbium-doped sodium yttrium fluoride luminescent composite nanophosphor (NaYF₄: Er³⁺ @ NaYF₄: Yb³⁺, Er³⁺), and cyclopentadiene
derivative AIE-active luminogen have been incorporated into the different polymer matrices to obtain the luminescent nanofibers. Carbon nanofibers have been also fabricated from polyacrylonitrile (PAN) using the electrospinning technique for optoelectronic devices, biological imaging, and photochemical reaction applications [9–33].

Among many polymers applied in solid-state lighting, it is decided to focus our attention on polyvinyl alcohol (PVA) as it is water soluble and biodegradable material. Its excellent properties such as thermal stability, chemical resistance, biocompatibility, hydrophilicity, emulsifying, adhesiveness, and inexpensiveness make it the material of choice for the luminescent nanofiber fabrication. PVA is a semicrystalline fiber, and its aqueous solution appears transparent and colorless. It also exhibits the unique film forming capability and nontoxic nature. PVA shows the potential applications in various fields such as biomedical applications and drug delivery [34–37]. Recently, researchers have keen interest in exploring the photoluminescence properties of PVA with its potential suitability for the electrospun nanofiber fabrication.

The development of electrospun photoluminescent nanofibers (PLNs) has gained much attention due to their potential applications in many fields such as solid-state lighting, nonlinear optical devices, and biological labels [38–42]. The incorporation of functional additives such as nanoparticles, nanophosphors, quantum dots, nanocrystals, and carbon quantum dots into polymeric nanofiber matrix is stunning which shows distinguishable luminescence, optical, magnetic, and electrical properties [43–45]. Specially, PLNs exhibit considerable significance when rare earth ions such as Eu³⁺, Er³⁺, Tb³⁺, and Tm³⁺ are doped into polymeric matrix. These PLNs are widely used in solid-state lighting applications including solid-state lasers, scintillators, and planar waveguides. Moreover, these polymeric nanofibers mats would be exceptionally interesting and fascinating structures because of their unique properties such as mechanical flexibility and very light weight [46–48]. It is observed that no studies have been done on fabrication of photoluminescent electrospun nanofibers of polyvinyl alcohol (PVA) with doping of NaYF₄: Eu³⁺ nanophosphor. Therefore, in the present paper, NaYF₄: Eu³⁺ nanophosphor/polyvinyl alcohol (PVA) composite nanofibers were prepared using electrospinning technique with different concentrations of NaYF₄: Eu³⁺ nanophosphor. Herein, we also focus on the morphology and photoluminescence properties of composite nanofibers at room temperature. The produced photoluminescent nanofibers (PLNs) would have potential usage in the solid-state lighting applications.

2. Experimental Methods

2.1. Materials. The rare earth yttrium oxide (Y₂O₃) and europium oxide (Eu₂O₃) of 99.99% purity have been used for the proposed study. Including sodium fluoride (NaF) (99.9%), sodium hydroxide (NaOH), hydrochloric acid (HCL), ethanol, distilled water, and polyvinyl alcohol (PVA), all chemicals were of analytical grade and used without further purification in the experiment.

2.2. Synthesis of NaYF₄: Eu³⁺ Nanophosphor. Eu₂O₃ and Y₂O₃ were dissolved in dilute HCl @ 60°C under constant magnetic stirring separately to prepare the stock solutions. 2 ml of 0.5 M sodium fluoride (NaF) solution is prepared in deionized water in a three neck flask and 2 ml chlorinated salt YCl₃, EuCl₃ aqueous solution also introduced in same flask. In a typical synthesis, NaOH (1.5 g) was mixed in ethanol (40 ml), which was added drop wise into three neck flask solutions with the help of burette under the constant magnetic stirring at 40°C. Reaction is kept under vigorously stirring for 1 h. At the end of the reaction, white colloidal precipitates were transferred to a 50 ml autoclave and heated at 180°C for 24 h. The autoclave was allowed to cool at room temperature, and precipitates were collected by centrifugation at 5000 rpm and washed with distilled water in sequence and dried in incubator at 100°C for 12 h. NaYF₄: Eu³⁺ nanophosphor was further used to fabricate the polymeric nanofiber mat of polyvinyl alcohol (PVA).

2.3. Electrospinning. The polymeric photoluminescent nanofibers (PLNs) have been fabricated via the electrospinning technique by using NaYF₄: Eu³⁺ nanophosphor and PVA. Figure 1 shows the schematic diagram for fabrication process of PLNs. As-prepared 20 mg NaYF₄: Eu³⁺ nanophosphor was dispersed in 4.6 g distilled water by ultrasonication for 1 h. Further, 400 mg PVA was introduced into the dispersed solution with a magnetic bead into the dispersed solution and kept under continuous stirring at room temperature for 16 h. The concentration of nanophosphor in solution was kept 5% with respect to PVA. Therefore, the homogeneous solution was achieved, which was filled in a 5 ml disposal syringe having a needle of nozzle size 24 G. A 13 × 14 cm aluminum sheet was wrapped on collector to get the well-aligned nanofibers. The syringe was placed at the stand of the electrospinning machine (ESPIN-NANO PICO, Chennai) to fabricate the electrospun nanofiber mat with parameters; distance between needle and collector 20 cm, flow rate 0.3 ml/h, collector speed 2000 rpm, and voltage of 15 kV. Consequently, well-aligned nanofibers were obtained on aluminum sheet which was wrapped on collector. Varied concentrations of nanophosphor (3, 5, and 8%) were used to fabricate the nanofiber mat.

3. Results and Discussion

3.1. Morphology of NaYF₄: Eu³⁺/Polyvinyl Alcohol Nanofibers. The morphology of electrospun fibers was characterized by scanning electron microscopy (SEM) using model ZEISS EVO 18. The morphology of well-aligned electrospun fibers can be seen easily in SEM micrographs, which depend directly upon the experimental set up of electrospinning machine. Model JEOL 2100F of high-resolution transmission microscopy (HRTEM) was used for further characterization of nanofibers. We cannot ignore the certain parameters which can affect the morphology of fibers during the experiment such as viscosity, conductivity, and concentration of the solutions as well as applied voltage, flow rate, collector speed, and distance between the needle of the syringe and collector. Figures 2(a)–2(c) show the SEM images of
NaYF₄: Eu⁺³/polyvinyl alcohol nanofibers @ 5%, respectively. Figure 2(d) is the HRTEM image of nanofibers which reveals that the nanophosphors were embedded homogeneously inside the PVA mat. The nanofibers were collected from the collector whose diameters were found to be in between 166 nm and 487 nm. Since the nanophosphor has

Figure 1: Schematic diagram for fabrication of polymeric photoluminescent nanofibers (PLNs) using electrospinning technique.

Figure 2: (a–c) show the SEM image of NaYF₄: Eu⁺³/polyvinyl alcohol nanofibers @ 5%, and (d) shows the HRTEM image of nanofibers and dotted circle exhibits the presence of particles of nanophosphor inside the nanofibers.
already been synthesized separately, therefore, the size of nanofibers does not affect the particle size (~35 nm) of nanoporphor. These nanoparticles were impinged successfully in PVA shell via the electrospinning technique. It is also observed that nanophosphor was incorporated into the polymer matrices without any change of photoluminescence properties of nanophosphor during the nanofiber fabrication via electrospinning. Photoluminescence properties (excitation/emission) can be affected by the use of material which is being doped into the host lattice of nanophosphor. Herein NaYF₄: Eu³⁺ nanoporphor synthesis, Eu is used as a dopant in NaYF₄ host lattice.

3.2. Photoluminescence (PL) of NaYF₄: Eu³⁺/Polyvinyl Alcohol Nanofibers. Photoluminescence (PL) spectra were recorded by spectrofluorometer model Perkin-Elmer LS 55. The emission spectrum of NaYF₄: Eu³⁺/polyvinyl alcohol nanofibers demonstrates the characteristic sharp peaks at 538 nm and 724 nm associated with the $^5D_0 \rightarrow ^7F_j$ transition of Eu³⁺ ion. 5% NaYF₄: Eu³⁺ was doped into the polyvinyl
alcohol to fabricate the nanofibers via electrospinning. These nanofibers display typical Eu^{3+} emission transition in the 500–725 nm regions [11]. Figure 3(a) shows the photoluminescence spectrum of down shift part of the nanofibers upon the excitation of 239 nm wavelength at room temperature. A hypersensitive red emission peak at 724 nm was observed in the red spectral region of the photoluminescence emission spectrum. Sharp red peak was ascribed to the electric dipole transition of the $^5D_0 \rightarrow ^7F_4$ transition. The emission peaks at 538 nm and 554 nm are due to the magnetic dipole transition of $^5D_0 \rightarrow ^7F_2$ [49]. It can be seen that magnetic dipole transition is lower than that the electric dipole transition. The PL emission spectrum shows that the Eu^{3+} ions are located at the noninversion symmetric sites [50–52]. Pure PVA photoluminescence emission peaks have been observed at 420 nm and 434 nm [34]. It can be observed that NaYF$_4$: Eu$^{3+}$ nanophosphor has enhanced the photoluminescence properties of nanofibers up to 724 nm. The International Commission on Illumination (CIE) 1931 has been used to draw the color space chromaticity diagram for the polymeric nanofibers. X-illumination (CIE) 1931 has been used to draw the color space chromaticity diagram for the polymeric nanofibers. Figure 3(b) represents the CIE diagram, which suggests the good color quality for understanding luminescence properties of the nanofibers containing Eu$^{3+}$ ions.

3.3. X-Ray Diffraction (XRD) and Raman Spectra of NaYF$_4$: Eu$^{3+}$/Polyvinyl Alcohol Nanofibers. X-ray diffraction characterization of nanofibers was performed by using XRD Rigaku Japan with X-ray source CuK$\alpha$ ($\lambda = 0.15418 \text{ nm}$). NaYF$_4$: Eu$^{3+}$/polyvinyl alcohol nanofibers were collected from aluminium foil (Al) which was used as a substrate for fiber deposition during the fascinating electrospinning technique. The cubic structure of NaYF$_4$: Eu$^{3+}$ nanophosphor has been decided with the help of JCPDS card no. 77-2042. The cubic crystal structure of NaYF$_4$ exhibits peaks at angles $2\theta = 28.85^\circ$ (111), 33.17° (200), 47.6° (220), 53.88° (311), 56.76° (222), 69.85° (400), 76.10° (331), and 79° (420) [11]. The XRD pattern of nanofibers is shown in Figure 4(a). According to JCPDS card no. 53-1857, the two diffraction peaks are observed at angles $\theta = 19.46^\circ$ and 22.32° which are attributed to PVA. The XRD pattern showed the other broad and sharp peaks at angles 28.96° (111), 33.50° (200), 48° (220), 56° (222), and 69.94° (400). The peaks observed at angles 38.30°, 44.52°, 65.04°, and 78.18° are attributed to Al foil [53, 54]. The XRD result shows that the peaks of nanophosphors are slightly shifted to right side due to the stress in PVA shell.

Renishaw spectrophotometer (micro-Raman model in Via Reflex) with $\lambda = 514 \text{ nm}$ laser excitation was used to record the Raman spectra of polymeric nanofiber. Raman spectra of NaYF$_4$: Eu$^{3+}$/polyvinyl alcohol nanofibers are shown in Figure 4(b). The electrospun nanofibers reveal the broad scattering peaks at 2917 cm$^{-1}$, 2745 cm$^{-1}$, and 1428 cm$^{-1}$ in the spectrum, which confirms the existence of polyvinyl alcohol (PVA), and the peaks are assigned to the stretching vibration of CH$_2$, CH, and OH, respectively [55, 56]. Nanophosphor has a discrete Raman spectrum in the 2565 to 2202 cm$^{-1}$ region, which exhibits the stretching modes of CH$_2$ [57]. The Raman spectra show that the scattering peaks of PVA are slightly shifted due to uniform impingement of nanophosphor into the PVA shell.

4. Conclusion

NaYF$_4$: Eu$^{3+}$/polyvinyl alcohol nanofibers were prepared successfully by using the electrospinning technique. The well-aligned photoluminescent nanofibers (PLNs) have average diameters from 166 to 487 nm. The SEM and HRTEM micrograph showed that NaYF$_4$: Eu$^{3+}$ nanophosphor is mixed homogeneously in the PVA matrix. The nanofibers exhibited considerable effect on its PL properties because of
the strong coordination interaction between nanophosphor and PVA. The enhanced intensity ratios \( {^3}D_0 \rightarrow {^3}F_0 \) to \( {^3}D_0 \rightarrow {^3}F_4 \) of the nanofibers showed more polarized chemical environment of Eu\(^{3+} \) ions. The PL spectra of NaYF\(_4\)·Eu\(^{3+}\)/PVA nanofibers showed the strong red emission due to its high emission intensity. These nanofibers are the best choice to illuminate the white light in solid-state lighting world.

**Data Availability**

The processed data cannot be shared at present time. Since the data is also the integral part of our ongoing research work with other polymers. However, findings of this research work will be provided from corresponding author on reasonable demand.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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