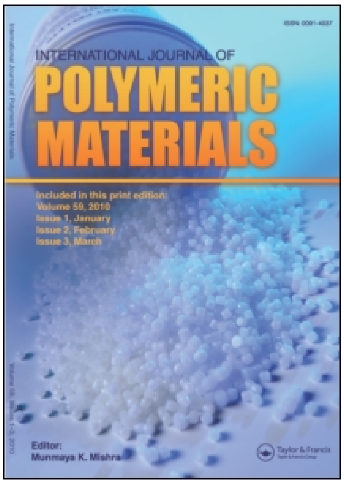

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Synthesis and Characterization of Electrospun Poly(ethylene oxide)/Europium-Doped Yttrium Orthovanadate (PEO/YVO_4:Eu^{3+}) Hybrid Nanofibers

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Europium-doped yttrium orthovanadate/polyethylene oxide nanofibers were fabricated by firstly, synthesizing crystalline YVO_4:Eu^{3+} nanoparticles using an aqueous precipitation method followed by electrospinning of PEO/YVO_4:Eu^{3+} polymer composites.

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X-ray diffraction patterns showed that the nanoparticles exhibited well-defined peaks that were indexed as the tetragonal phase of YVO_4. No additional peaks of other phases were observed indicating that Eu^{3+} ions were effectively built into the YVO_4 host lattice. The photoluminescence spectra for the nanofibers showed peaks at 593, 615, 650, and 698 nm which was ascribed to the $^5D_{0-}{}^7F_1$, $^5D_{0-}{}^7F_2$, $^5D_{0-}{}^7F_3$ and $^5D_{0-}{}^7F_4$ transitions of Eu^{3+}. Due to an efficient energy transfer from vanadate groups to Eu^{3+}, the composite nanofibers showed a strong red emission under ultraviolet excitation characteristic of the red luminescence of the europium ion. The results demonstrate that this synthetic approach could prove to be viable for the fabrication of rare earth/polymer composite nanofibers intended for luminescent device applications.

Keywords electrospinning, luminescence, nanofibers, $YVO_4:Eu^{3+}$

INTRODUCTION

Much attention has been paid recently to rare-earth-doped materials which are an important type of phosphor due to their excellent performance in many areas such as high-performance magnets, luminescence devices and catalysts [1]. Among these rare-earth-doped materials, europium-doped yttrium orthovanadate ($YVO_4:Eu^{3+}$) has been widely applied in many fields. In fact, by partial replacement of VO_4^{3-} ions with PO_4^{3-} ions, a new series of europium-doped yttrium phosphate-vanadates ($YV_{1-x}P_xO_4$) has emerged with better luminescent properties. Rare earth ion-doped yttrium orthovanadate phosphors, such as $YVO_4:Eu^{3+}$, have been extensively applied in luminescence and displays, such as light phosphor powders, field emission displays (FEDs), cathode ray tubes (CRTs), and plasma display panels (PDPs), as well as high-pressure mercury lamps [2–4]. It has been extensively reported that photonic structures with wavelength scale dimensions offer interesting opportunities to engineer the optical properties of light-emitting materials [5, 6]. Particularly for dimensions approaching the wavelength of light, the associated strong modification of the local photonic density of states alters the photo-physical properties of the emitters [7]. In comparison with bulk materials, the shape of a one-dimensional structure provides a better model system to investigate the dependence of electronic transport and optical properties on size confinement and dimensionality. Therefore, the design and preparation of one-dimensional nanostructured materials in which luminescent materials are embedded has attracted a great deal of attention in recent years [8–13]. To achieve the one-dimensionality of the structures, electrospinning, a technique based on the use of electrostatic forces to draw a polymer solution into nanofibers, has been an indispensable tool due to its convenient, inexpensive and superior characteristics. A major advantage of electrospinning is the possibility to produce hybrid functional materials by incorporating luminescent material into the nanofibers [8, 9, 14]. The polymer, the luminescent material and the characteristic size of the structures can be varied independently, therefore allowing for a wide range of applications. Despite growing importance, the optical properties of light emitters embedded in polymer nanofibers have so far not been explored in depth due to technological challenges in obtaining continuous fibers with diameters in the range of the wavelength of light. In light of this, we attempt in this paper the synthesis and characterization of one-dimensional hybrid nanofibers of PEO/YVO_4:Eu^{3+} by a combination of aqueous precipitation reactions and electrospinning. To the best of our knowledge, this is the first time that YVO_4:Eu^{3+} particles are embedded in PEO and reported in the open literature.

EXPERIMENTAL

Synthesis

10 ml of a 0.1 M aqueous solution of sodium orthovanadate (Na_3VO_4) was prepared by dissolving 1 equivalent of sodium metavanadate ($NaVO_3$) in an aqueous solution containing 3 equivalents of NaOH. The pH was adjusted to 13 using NaOH to ensure complete transformation of the metavanadate into orthovanadate. A 10 ml aliquot of a 0.1 M aqueous solution of $Y(NO_3)_3$ and $Eu(NO_3)_3$ was added dropwise. A white precipitate formed instantly, a pH of 12.25 was observed after 30 min. 0.25 g of sodium metaphosphate ($NaPO_3$) was then added to the solution formed before agitation in an ultrasonic bath for 12 h. The solution was then oven-dried for complete removal of solvent to obtain YVO_4:Eu^{3+} powder. 10 wt% polyethylene oxide (PEO, Sigma Aldrich, $M_w = 300{,}000$) was prepared in deionized water to which 0.25 g of YVO_4:Eu^{3+} powder was added before stirring for 24 h. This final solution of (PEO)/ YVO_4:Eu^{3+} was then ready for electrospinning.

Electrospinning Set-Up

The electrospinning set-up used in this work has been reported in our previous work [14]. In the set-up the solution to be electrospun was loaded into pasteur pipettes, held horizontally and fitted over a positive electrode lead connected to a high voltage power supply that can generate DC voltages up to 25 kV. A copper wire was inserted into the pasteur pipette to act as the electrode for charging the polymer solution. Grounded aluminum foil stuck on a perspex board was placed 15 cm away from the pipette tip. Three substrates, silicon, plain glass and glass on which one side was coated with a thin film of fluorine-doped tin oxide, were stuck on the aluminum foil to collect the electrospun nanofibers for characterization. Electrospinning was carried out in air at applied voltages that ranged from 5 kV to 20 kV.

Characterization

The morphology of the fibers was studied using two microscopes, a Leo-StereoScan 440 and a Vega Tescan scanning electron microscope. Transmission electron microscopy (TEM) was carried out on a JOEL 1210. The samples for TEM were prepared by depositing a drop of colloidal material solution on a carbon grid. Photographs were taken using a single shot digital camera (Sony DSC – S730 Cyber-shot). Ultraviolet-visible (UV-VIS) spectra were recorded on a Varian 500 UV-Vis/NIR spectrophotometer. Fourier transform infrared spectroscopy spectra were obtained using a Perkin Elmer Pragon 1000PC FTIR spectrometer. Photoluminescence (PL) spectra were recorded on a Varian Eclipse spectrofluorometer. The X-ray diffraction (XRD) patterns of the samples were obtained on a Bruker AXS D8 Advance diffractometer using Cu Kα radiation ($\lambda = 1.5406$Å).

RESULTS AND DISCUSSION

Scanning and Transmission Electron Microscopy

The TEM overview image of the YVO_4 nanocrystals is shown in Figure 1(a). The particles have a raisin-like morphology and an average diameter of less than 100 nm confirming the successful synthesis of the nanoparticles. Figure 1(b) shows the scanning electron micrograph of pure PEO electrospun nanofibers. The fibers are randomly oriented and there exist many curvatures along the axis of fibers, which might be attributed to the asynchronous deposition of different parts of the electrospun fiber because of its own instabilities, such as whipping or non-axisymmetric instability [15]. The major contributing factor to the random orientation of fibers is bending instability which is chiefly due to repulsive electrostatic forces brought about by the induced surface charges. The bending becomes more pronounced when the fiber diameter decreases. In the same vein, Figures 1(c) and (d) show SEM images of (PEO)/YVO_4:Eu^{3+} hybrid nanofibers deposited on different collectors. It can be seen that the fibers were collected in random orientation because of bending instability associated with the spinning jet. On using a rotating collector there was a significant improvement in the axial alignment of the fibers. A combined effect of improved drying and stretching due to the rotating collector resulted in smooth fibers with an average diameter of 300 nm compared to an average 400 nm on the static collector. The combined effect of a high spinning voltage, the low surface tension of ethanol and the high concentration of PEO are believed to be the major contributing factors to fiber formation. Splaying was observed at 17.5 kV which facilitated solvent evaporation on a thinner jet, allowing increased surface charges and thus a greater electrostatic force to overcome the surface tension.

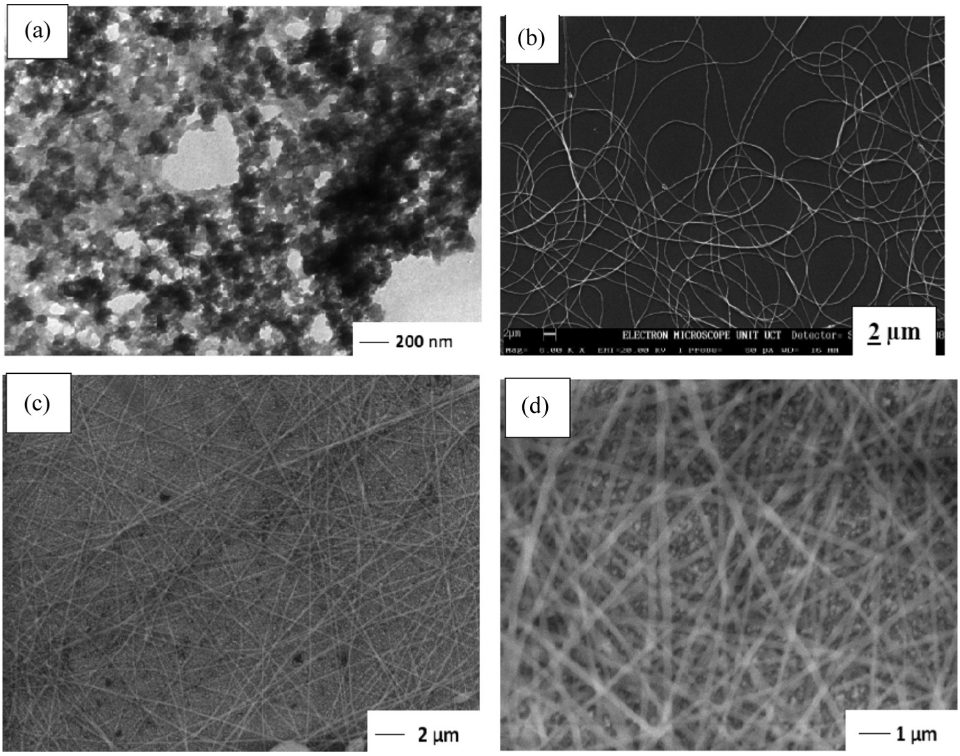

Figure 1: (a) TEM image of YVO_4:Eu^{3+} nanoparticles. SEM images of electrospun pure PEO and (b) PEO/YVO_4:Eu^{3+} hybrid nanofibers collected at 17.5 kV (c) 20 kV (d).

FTIR Spectroscopy

Figure 2 shows the FTIR spectra of the pure PEO nanofibers, YVO_4:Eu^{3+} powder and the PEO/YVO_4:Eu^{3+} hybrid nanofibers. The FTIR spectra of PEO nanofibers show a strong band near 2900 cm^{-1} attributed to the symmetric and asymmetric C–H stretching modes. The bands at about 1456 and 1350 cm^{-1} are attributed to the vibrations of $–CH_2–$ group and the bands at about 1102 and 962 cm^{-1} are assigned to the asymmetric stretching vibration of the C–O group [16]. The FTIR spectrum of the YVO_4:Eu^{3+} powder shows typical spectral characteristic of VO_4^{3-} with a strong IR band in the range of 780–920 cm^{-1}(13). In addition, weak frequencies in the ranges 2900–3500 and 1100–1670 cm^{-1} could be attributed to C−H, C−O and O−H vibration bands [17]. Weaker bands observed at 1100–2100 cm^{-1} could suggest the absorption of H_2O and CO_2 from the atmosphere since the spectra were not obtained under controlled atmosphere. Comparing the spectra, one could notice that the vibration band at 2900 cm^{-1} (C−H), 1456 and 1350 cm^{-1} ($-CH_2$) of pure PEO fibers shifted to about 2902, 1460 and 1333 cm^{-1} in the spectrum of PEO/YVO_4:Eu^{3+} hybrid nanofibers. In addition, the width of the band broadened and the intensity became stronger

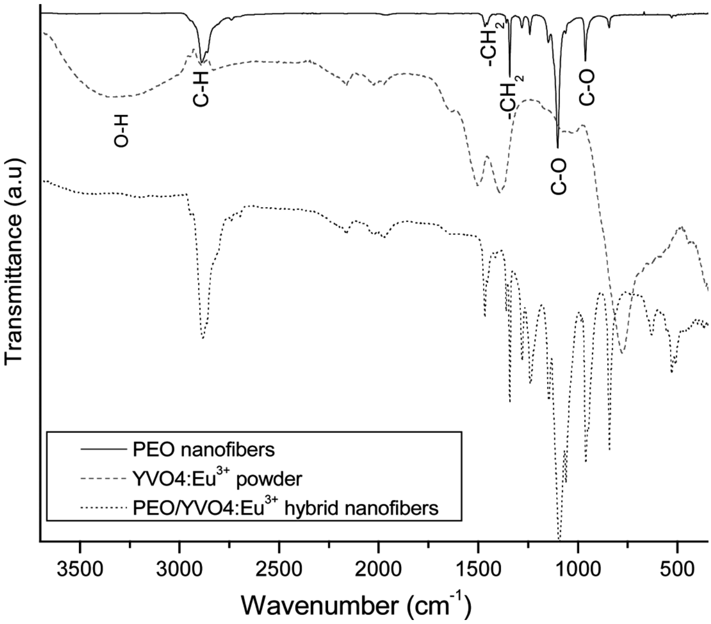

Figure 2: FTIR spectra of PEO nanofibers, YVO_4:Eu^{3+} nanoparticles powder and PEO/YVO_4:Eu^{3+} nanofibers.

for the PEO/YVO_4:Eu^{3+} hybrid nanofibers. This observation suggested that there were some interactions between the PEO molecules and the YVO_4:Eu^{3+} through the coordination of Eu^{3+} ions to the $C=O$ groups of PEO. These interactions are strongly believed to be responsible for the luminescent properties of the hybrid nanofibers. Just of recent, similar observations were reported in the study of poly(vinyl pyrrolidone)/Eu^{3+} hybrid nanofibers [9].

X-Ray Diffraction Measurements

Figure 3 shows the XRD pattern obtained on the YVO_4:Eu^{3+} powder in order to establish the crystallinity of the nanoparticles. The pattern is in agreement with the usual zircon-type structure of $EuVO_4$ or YVO_4 [2,18]. Well-defined diffraction peaks appear, all of which can be indexed as the tetragonal phase of YVO_4 which are consistent with the literature data (JCPDS No. 17-0341). No additional peaks for other phases were observed indicating that Eu^{3+} ions were effectively built into the YVO_4 host lattice. This observation confirms that experimental conditions were optimal for the almost exclusive precipitation of YVO_4 instead of $Y(OH)_3$. The nanoparticle size was estimated from the Scherrer equation $D = 0.941\lambda/\beta \cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm) and θ and β are the diffraction angle and full width at half-maximum of an observed peak, respectively

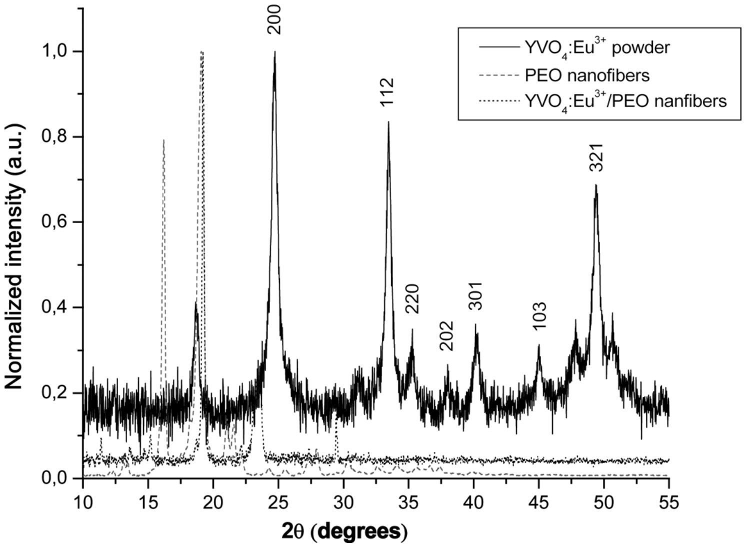

Figure 3: X-ray diffraction pattern (Cu Kα) for YVO$_4$:Eu^{3+} nanoparticles (powder), PEO/YVO$_4$:Eu^{3+} nanofibers and PEO nanofiber.

[18]. In this work, the strongest peak (200) at $2\theta = 25.0°$ was used to calculate the average nanoparticle size (D). The roughly estimated nanoparticle size is 9.53 nm for our particle with raisin-like morphology. A similar rough calculation by Zhu et al. [2] gave 16 nm as average size for spindle-like particles. The marked difference may be due to the different methods of preparation and the morphology of the particles. In addition, from the XRD pattern of Figure 3, for pure PEO nanofibers, the diffraction peaks at $2\theta = 19.35$ and 22.55° correspond to the PEO crystalline phase. This is in agreement with the report of Yan et al. (19). From the peaks corresponding to the YVO$_4$:Eu^{3+} nanoparticles, it can be seen that the YVO$_4$:Eu^{3+} is essentially crystalline. In the resulting PEO/YVO$_4$:Eu^{3+} hybrid nanofibers, the diffraction peaks of YVO$_4$:Eu^{3+} at 13.5, 19.35, and 22.55 could be seen which suggests the presence of PEO/YVO$_4$:Eu^{3+} hybrid nanofibers, hence could be responsible for the luminescence of the material. The identification of these peaks could equally be attributed to the change in the crystalline phase of the YVO$_4$:Eu^{3+} in the hybrid nanofibers due to the molecular interactions between the YVO$_4$:Eu^{3+} molecules and the oxygen atoms on the PEO chain.

UV-Vis Measurements

UV-vis absorption spectra of the PEO/YVO$_4$:Eu^{3+} nanofibers and the YVO$_4$:Eu^{3+} powder (Figure 4(a)) show a broad band from 250 to 300 nm with a peak around 280 nm attributed to the charge transfer from the oxygen

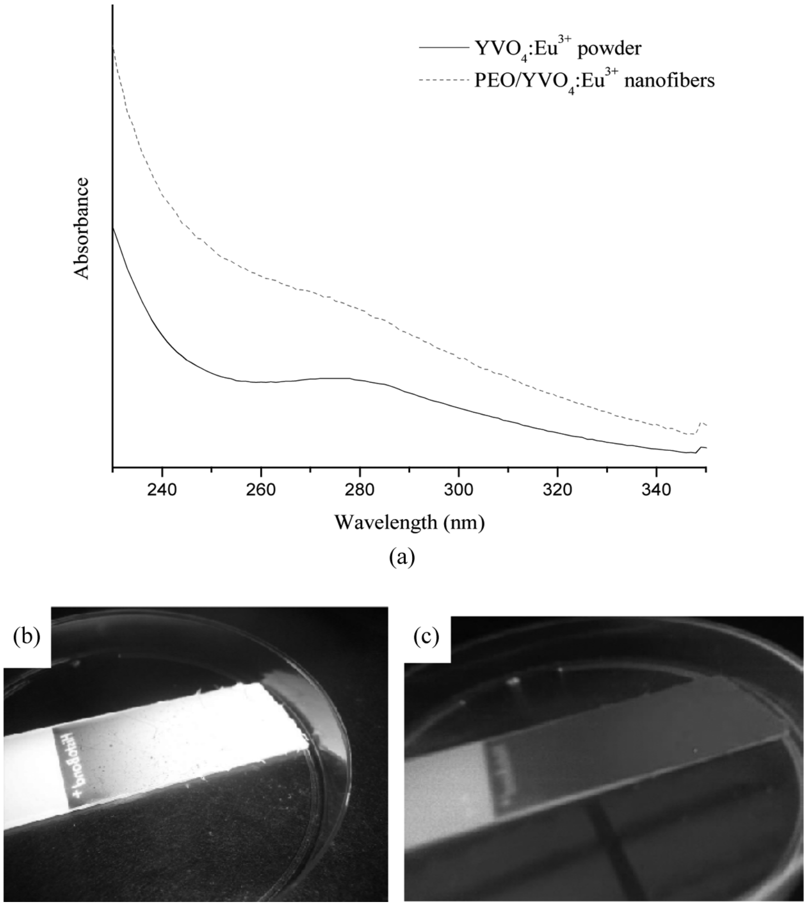

Figure 4: (a) UV absorption spectrum of YVO$_4$:Eu^{3+} nanoparticles and PEO/YVO$_4$:Eu^{3+} nanofibers (inset: Photographs of PEO/YVO$_4$:Eu^{3+} nanofibers (b) before UV illumination and (c) after UV illumination).

ligands to the central vanadium atom inside the VO_4^{3-} group. Under short wavelength UV irradiation, YVO$_4$:Eu^{3+} exhibits red emission. It was therefore expected that PEO/YVO$_4$:Eu^{3+} nanofibers would exhibit red emission under UV excitation as shown in the photographs of Figure 4(b) and (c). The red light emission of nanofibers upon excitation at 254 nm with a UV lamp confirms that a red phosphor material was successfully embedded in the polymer nanofibers.

PL Measurements

Samples of PEO/YVO$_4$:Eu^{3+} hybrid nanofibers and YVO$_4$:Eu^{3+} powder were dispersed in ethanol with an ultrasonic bath before photoluminescence

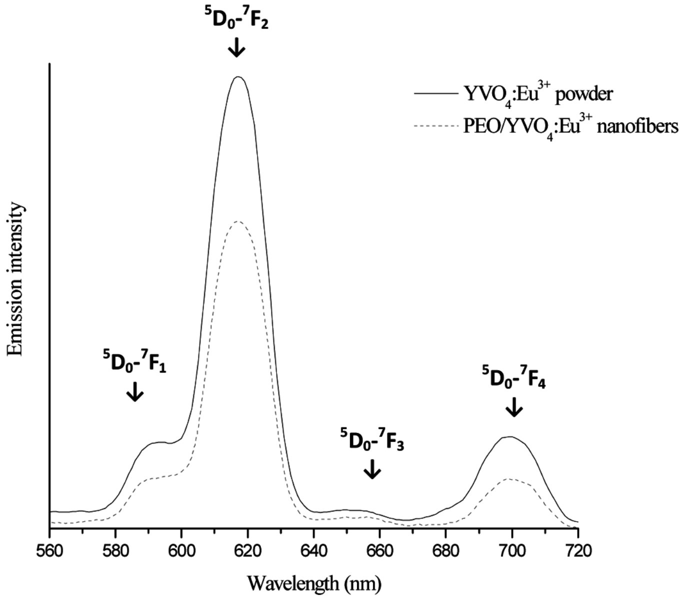

Figure 5: PL spectra of YVO$_4$:Eu^{3+} powder and PEO/YVO$_4$:Eu^{3+} nanofibers.

(PL) recorded by a fluorescence spectrometer at room temperature. Figure 5 shows the photoluminescence excitation spectra of PEO/YVO$_4$:Eu^{3+} nanofibers and YVO$_4$:Eu^{3+} powder that were excited at 290 nm. The spectra are dominated by the emission from europium ions, and mainly the $^5D_0$-$^7F_2$ and $^5D_0$-$^7F_4$ forced electric-dipole transitions for which high intensities are a consequence of the absence of an inversion symmetry at the Eu^{3+} lattice site (D_{2d} symmetry). Other contributions of weaker importance are the $^5D_0$-$^7F_1$ and $^5D_0$-$^7F_3$ magnetic dipole transitions. The Eu^{3+} shows a strong photoluminescence, dominated by the $^5D_0$-$^7F_2$ red emissions at 614 nm due to an efficient energy transfer from the vanadate group to Eu^{3+}. Similar observations have been reported by Zhu et al. (2). This confirmed that YVO$_4$:Eu^{3+} was successfully embedded in the nanofibers thereby making it a suitable candidate for color display panels. The difference in intensities was expected as the PEO has a dilution effect.

CONCLUSIONS

In summary YVO$_4$:Eu^{3+} nanocrystals were successfully synthesized using aqueous precipitation. The nanocrystals were successfully embedded in polyethylene oxide (PEO) nanofibers thus PEO/YVO$_4$:Eu^{3+} hybrid nanofibers were successfully synthesized by electrospinning. It was successfully demonstrated that it is possible to fabricate rare earth/polymer hybrid nanofibers with ordered architectures using a simple electrospinning set-up. This work therefore indicates a facile route for the development of luminescent nanomaterials that are useful in luminescent device applications.

REFERENCES

[1] Yu, H., Song, H., Pan, G., Li, S., Liu, Z., Bai, X., Wang, T., Lu, S., and Zhao, H. *J. Lumin* **124**, 39 (2007).

[2] Zhu, L., Li, J., Li, Q., Liu, X., Meng, J., and Cao, X. *Nanotechnology* **18**, (2007) DOI: 10.088/0957-4484/18/5/055604.

[3] Huang, Y., Quan, X. F., Wei, Q. Q., and Lieber, C. M. *Science* **291**, 851 (2001).

[4] Bachtold, A., Hadley, P., Nakanishi, T., and Dekker, C. *Science* **294**, 1317 (2001).

[5] Bockrath, M., Liang, W., Bozovic, D., Hafner, J. H., Lieber, C. M., Tinkham, M., and Park, H. *Science* **291**, 283 (2001).

[6] Shen, Y., and Prasad, P. N. *Appl Phys B* **74**, 641 (2002).

[7] Wang, X. Y., Drew, C., Lee, S. H. Senecal, K.J., Kumar, J., and Samuelson, L. A. *Nano Lett* **2**, 273 (2002).

[8] Hou, Z., Yang, P., Li, C., Wang, L., Lian, H., Quan, Z., and Lin, J. *Chem. Mater.* **20**, 6686 (2008).

[9] Tang, S. S., Shao, C. L., and Li, S. Z. *Chin Chem Lett* **18**, 465 (2007).

[10] Takeshita, S., Isobe, T., and Niikura, S. J. *Lumin* **128**, 1515 (2008).

[11] Lee, C. I., Lim, J. S., Kim, S. H., and Suh, D. H. *Polymer* **47**, 5253 (2006).

[12] Huignard, A., Buissette, V., Franville, A,-C., Gacoin, T., and Boilot, J. P. J. *Phys. Chem. B.* **107**, 6754 (2003).

[13] Zhang, H., Fu, X., Niu, S., Sun, G., and Xin, Q. J. *Solid State Chem* **177**, 2649 (2004).

[14] Ajao, J. A., Abiona, A., Chigome, S., Kana Kana, J. B., and Maaza, M. J. *Mater. Sci.* **45**, 713 (2010).

[15] Deitzel, J. M., Kleinmeyer, J., Hirvonen, J. K., and Beck, T. N. C. *Polymer* **42**, 8163 (2001).

[16] Sui, X., Shao, C., and Liu, Y. *Polymer* **48**, 1459 (2007).

[17] Boyer, D., Bertrand-Chadeyron, G., Mahiou, R., Caperaa, C., and Cousseins, J. C. J. *Mater. Chem.* **9**, 211 (1998).

[18] Nanda, J., Sapra, S., and Sarma, D. D. *Chem. Mater.* **12**, 1018 (2000).

[19] Yan, E., Wang, C., Huang, Z., Xin, Y., and Tong, Y. *Mater Sci Eng A* **59**, 464 (2007).