Journal of Colloid and Interface Science 400 (2013) 175–180

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

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Preparation of aligned Eu(DBM)$_3$phen/PS fibers by electrospinning and their luminescence properties

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ARTICLE INFO

Article history:
Received 16 January 2013
Accepted 14 March 2013
Available online 22 March 2013

Keywords:
Electrospinning
Continuous
Super-long
Aligned composite fibers
High molecular weight polymer
Low speed rotating drum
Sonochemical method
Europium complex
Fluorescence lifetime
Photoluminescence stability

ABSTRACT

Electrospinning is a technique employed to prepare nanofibers of polymer, ceramics, and composite that are used in the high electrostatic field. Alignment is an important step toward the exploitation and applications of these fibers. In the present report, super-long aligned luminescent composite Eu(DBM)$_3$phen/PS fibers (DBM = dibenzoylmethane, phen = 1,10-phenanthroline, PS = polystyrene) were prepared via an electrospinning method. The key to the success of this method was the usage of high molecular weight PS ($M_w = 4.4 \times 10^5$) in the electrospinning solution and the low speed (>0.5 m/s) collecting drum. Luminescent properties of the composite fibers were systemically studied in comparison with that of the corresponding pure europium complex Eu(DBM)$_3$phen. The results showed that the fluorescence lifetime of $^5D_0$ state and the luminescent intensity of Eu^{3+} in Eu(DBM)$_3$phen/PS composite fibers increased gradually with the fiber diameter. The composite fibers with smaller diameter exhibited better photoluminescence stability than that of the pure complex Eu(DBM)$_3$phen.

1. Introduction

Electrospinning is a simple, versatile, and useful technique for fabricating nanofibers that are exceptionally long in length, uniform in diameter from a rich variety of functional materials [1–3]. The obtained fibers from electrospinning are usually a random mat without structural orientation [4,5]. Their diameters are in the range from over ten nanometers to a few microns. Though the method of electrospinning has been known for a long time and is fairly straightforward, controlled production of aligned fibers reproducibly on a substrate remains a major challenge in this area [6–8]. The electrospun fibers arranged randomly on the substrate cannot meet the requirement for practical applications due to their ununiformity of mechanical and optoelectronic properties; thus, the uniformly aligned electrospun fibers are preferable in order to develop novel applicable functional materials.

In recent years, the spun fibers with regularly arrayed structures were demonstrated by using various collectors, such as high speed rotating drum and sharp edge of a thin rotating wheel, which are metal frames introducing an auxiliary gap between the collector and the syringe needle [9–13]. Among these collectors, only the rotating drum can satisfy the requirements of producing seriate, uniform and aligned fibers, but the others induce relatively short tows of aligned fibers. Doshi and Reneker have showed that aligned fibers could be obtained using the collagen solution with a concentration of 0.0083 g/ml during electrospinng process when the linear speed of rotating drum was about 1.4 m/s [9]. Jose et al. have reported that aligned PLGA/collagen/HA composite fibers were obtained using rotating drum with the linear speed of 8.0 m/s, when the concentrations of the electrospinning solution was 10.0 wt.% [14].

In recent years, there is growing interest in exploring novel one-dimensional luminescent nanostructure materials, since they exhibit specific and fascinating luminescent properties such as various emission lifetimes and increased luminescence efficiencies, which are different from those of their bulk counterparts [15–17]. The electrospinning technique is also developed to prepare lanthanide oxide nanowires, as well as composite nanowires of organic-RE complex compounds [18–24]. Recently, we have employed this technique to prepare randomly arranged Eu(DBM)$_3$phen/PS composite fibers (DBM is dibenzoylmethane, phen is 1,10-phenanthroline, and PS is polystyrene). The average diameter of the obtained fibers is about 300 nm. The radiative transition properties of Eu^{3+}:$^5D_0$ level including transition rates, fluorescence branching

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0021-9797/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2013.03.017

ratios, and radiative transition lifetime were calculated [25]. However, as mentioned above, these randomly arranged fibers cannot be used in practical applications, since it often requires well aligned and highly ordered architectures in fields of microelectronics and photonics [7,8].

In the present work, the uniformly aligned Eu(DBM)$_3$phen/PS composite fibers were prepared by varying the parameters of electrospinning experiment. Two key parameters which might influence the architecture of the products were changed simultaneously. One is that the sonochemical-synthesized high molecular weight polystyrene, which could increase the viscosity of elctrospinning solution, was used. Moreover, the other is that a low speed rotating collecting drum, which could result in the deposition of Eu(DBM)$_3$phen/PS composite fibers into the linear and parallel arrays, was adopted. It was found that seriate and uniformly aligned Eu(DBM)$_3$en/PS composite fibers could be easily obtained when the speed of rotating drum was over 230 rpm corresponding to a linear speed of approximately 0.5 m/s. Average diameter of the aligned Eu(DBM)$_3$phen/PS composite fibers prepared with this method was smaller than 5 μm, and their lengths were dozens of centimeters. To the best of our knowledge, it is the first report of obtaining the seriously aligned fibers from the solution of high molecular weight polymer solution via the electrospinning technique with a low speed rotating drum.

In addition, the luminescence properties of these fibers were also studied in comparison with that of the relevant pure europium complex. It is interesting that the room temperature fluorescence lifetime for the $^5D_0$ level of Eu^{3+} in the composite fibers considerably became longer compared to that in the pure europium complex and was increased gradually with the diameter of the composite fibers. The photoluminescence stability of Eu^{3+} in the composite fibers with small diameter was improved compared to that of pure Eu(DBM)$_3$phen.

2. Experimental

2.1. Sample preparation

Europium complex (Eu(DBM)$_3$phen) was synthesized according to the reported method [26,27]. High molecular weight polystyrene was synthesized using sonochemical route [28]. For the sake of comparison, the low molecular weight polystyrene was also prepared using an emulsifier-free emulsion polymerization method [29]. In order to prepare seriately aligned composite fibers, 0.5%, 1%, and 2% w/w solutions of the high molecular weight PS in N, N-dimethylformamide (DMF) and tetrahydrofuran (THF) were used. An appropriate amount of Eu(DBM)$_3$phen was dissolved into the prepared 0.5%, 1%, and 2% w/w solutions of high molecular weight PS, respectively, and the mass ratio of Eu(DBM)$_3$phen complex to PS was 1:100 in all solutions (see Table 1). These solutions were stirred in order to make them uniform. The final solutions were then electrospun to produce composite fibers of Eu(DBM)$_3$phen complex and PS. The Eu(DBM)$_3$phen/PS composite fibers, which were electrospun from 0.5, 1.0 and 2.0 wt.% of PS solutions, were labeled as Eu/PS-1, Eu/PS-2, and Eu/PS-3, respectively. The compositions of the solutions are listed in Table 1. The schematic diagram of the electrospinning setup is shown in Fig. 1, which consisted of three major parts: a high-voltage power supply, a spinneret (plastic needle), and a collector (rotating plastic drum). In a typical electrospinning process, a solution was pumped through a nozzle, to which a high voltage relative to collector was applied, to form an electrically charged jet of solution. The solution jet was solidified on the collector with the accompanying evaporation of solvent. In the present electrospinning experiment, the applied voltage was 12.5 kV and the collection distance was 10 cm. Rotating speeds of the drum were adjusted to around 170–360 rpm corresponding to linear speed of about 0.4–0.9 m/s. In addition, the composite fiber mat consisting of Eu(DBM)$_3$phen complex and low molecular weight PS was also prepared under the same experimental conditions using 1 wt.% Eu(DBM)$_3$phen in PS solution.

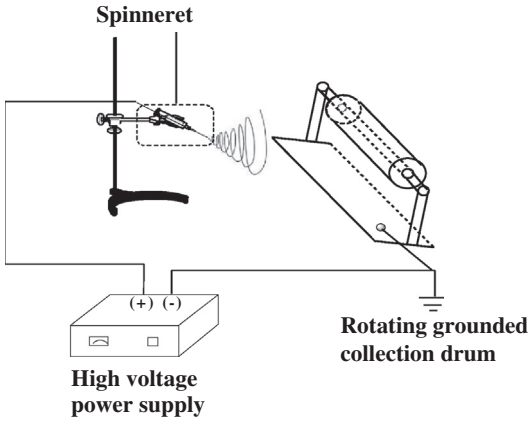

Fig. 1. Schematic diagram of the electrospinning setup.

2.2. Measurements

The molecular weight (M_w) of PS was determined by using high temperature gel permeation chromatography (GPC). A PL-GPC 220 high temperature gel permeation chromatography system (Polymer Laboratories Ltd.) with an online PD2040/DLS laser light scattering detector (Precision Detectors Inc.) and three PLgel 13 μm Olexis columns (300 × 7.5 mm) was used. The eluent was 1,2,4-trichlorobenzene (TCB, Acros) stabilized with 5×10^{-4} g/mL 2,6-ditert-butyl-4-methylphenol (BHT, Acros) and was filtered through membrane with a pore size of 0.2 μm prior to using. The injection volume was 200 μL, and the flow rate was 1.0 mL/min. The measurements were performed at 150 °C. The size and morphology of the composite fibers were determined on a Hitachi JSM-6360 scanning electron microscope. Fourier transform infrared (FTIR) spectra were recorded on a TENSOR 27. The excitation and emission spectra and fluorescence dynamics were recorded on a Hitachi F-4600 spectrophotometer using continuous 150 W Xe arc lamp radiation at room temperature. The emission spectra were measured under the same experimental conditions (excitation split, 2.5 nm; emission split, 2.5 nm; PMT voltage, 400 V). In the experiments of

Table 1
Composition of electrospinning solution.

Sample	Concentration of Eu complex or PS in electrospinning solution		Ratio of Eu complex to PS in Eu(DBM)$_3$phen/PS composite fibers (w/w)
	Concentration of Eu complex in DMF and THF	Concentration of high molecular weight PS in DMF and THF	
Eu/PS-1	0.005 wt.%	0.5 wt.%	1:100
Eu/PS-2	0.010 wt.%	1.0 wt.%	1:100
Eu/PS-3	0.020 wt.%	2.0 wt.%	1:100