



Luminescent polymethacrylate composite nanofibers containing a benzoic acid rare earth complex: Morphology and luminescence properties



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ABSTRACT

In this study, we systematically investigated the morphologies and luminescence properties of luminescent polymethacrylate composite nanofibers containing a benzoic acid rare earth complex. The analysis results indicated that the benzoic acid rare earth complex, Tb(4-methylbenzoic acid)₃phen, was distributed uniformly in the polymethacrylate nanofibers, which were fabricated by electrostatic spinning. The Tb(4-methylbenzoic acid)₃phen content in the polymethacrylate nanofibers was as high as 20% (mass%). The emission peaks of the as-prepared polymethacrylate composite nanofibers corresponded to the characteristic ⁵D₄–⁷F_{6, 5, 4, 3} transitions of Tb³⁺ ions. The highest emission peak was observed at 548 nm and corresponded to the ⁵D₄–⁷F₅ transition. When the Tb(4-methylbenzoic acid)₃phen content was less than 1%, even a 0.2% increase in the content increased the fluorescence intensity markedly. The thermal stability of the rare earth complex was higher in the as-prepared nanofibers; the initial decomposition temperature of the polymethacrylate composite nanofiber reached 291 °C. Composite nanofibers with different morphologies exhibited different luminescence characteristics. The fluorescence intensity and emission lifetime of porous nanobeads were nine and two times higher, respectively, than those of smooth nanofibers. The better morphological and luminescence properties exhibited by the synthesized luminescent polymethacrylate composite nanofibers should result in the use of benzoic acid rare earth complexes in a greater number of applications.

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1. Introduction

Significant attention is being devoted to designing and synthesizing novel luminescent materials with one-dimensional (1D) nanostructures, since they show unique luminescence characteristics and could be of potential use in a variety of applications [1–3]. It has been reported previously that luminescent materials distributed within 1D nanostructures exhibit better luminescence performances, including higher luminescence intensity, emission lifetimes, and luminescence efficiencies, than do their bulk counterparts [4]. Luminescent porous nanofibers can be used as oil-absorbing materials, while 1D nanotubes that exhibit luminescence can be used as drug carriers [5]. The amount of oil absorbed or drug released can be reliably monitored from the change in the luminescence intensity of these materials. Moreover, these materials can

also be used in the fields of microelectronics [6], photonics [7], displays [8], and sensors [9].

So far, a number of methods have been demonstrated for fabricating 1D nanomaterials, such as vapor deposition [10], laser ablation [11], and template-based techniques [12]. However, these methods are too complex to be applied widely. Electrospinning is an effective method developed in recent years for preparing 1D luminescent nanostructures in the form of nanowires, nanorods, nanofibers, nanobelts, nanotubes, and nanorings from various materials [13–15]. The electrospinning apparatus includes a high-voltage generator, plastic syringes, a nozzle, and a collector. During the electrospinning process, an electric force is employed to drive the solution or melt and form the nanofibers [16,17].

Benzoic acid rare earth complexes not only exhibit good coordination and matching energy levels but also exist in a variety of conjugate structures [18]. Further, these complexes have better luminescence properties. However, such complexes are difficult to produce directly and are usually formed through processes such as blending, extrusion, molding, and calendaring, owing to their

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poor thermal stability and tendency to accumulate in the composite matrix. These disadvantages limit the large-scale application of benzoic acid rare earth complexes. Recently, Liu et al. prepared poly(vinylpyrrolidone) nanofibers with $[\text{Ru}(4,7\text{-diphenyl-1,10-phenanthroline})_2(\text{dipyrido}[3,2\text{-}a:2',3'\text{-}c]\text{phenazine})]\text{Cl}_2$ using the electrospinning technique [19]. Yu et al. prepared polystyrene fibers with $\text{Eu}(\text{dibenzoylmethane})_3(1,10\text{-phenanthroline})$ by electrospinning [20]. Further, Wen et al. fabricated core–sheath luminescent fibers containing a $\text{Eu}(2\text{-thenoyltrifluoroacetone})_3(1,10\text{-phenanthroline})$ complex using the electrospinning method [21]. During the electrospinning of these polymer-based composite nanofibers, the processing temperature was close to the room temperature, and the organic rare earth complexes were distributed uniformly in the nanofibers. Hence, their fluorescence intensities, fluorescence lifetimes, and luminescence quantum efficiencies were high. Therefore, such materials are highly suited for use in various fields, including for protective clothing [22], magnetism and luminescence sensors [23], optical communication devices [24], and in defense, security, and environmental engineering-related fields [25]. However, there have been few reports on the mechanism by which the benzoic acid rare earth complexes are dispersed in the polymer-based nanofibers. Further, the effects of the structure of the nanofibers on their luminescence properties, and, in particular, those of the morphology of the nanofibers on the fluorescence intensity and fluorescence lifetime, have not been elucidated systematically.

With this goal in mind, in this study, we investigated the relationship between the structure of luminescent composite nanofibers and their luminescence characteristics. A benzoic acid rare earth complex, $\text{Tb}(4\text{-methylbenzoic acid})_3\text{phen}$, and poly(methyl methacrylate) (PMMA) were used as the luminescent material and polymer, respectively. A series of luminescent nanofibers of the PMMA composite were prepared by electrospinning. The mechanism by which the benzoic acid rare earth complex was dispersed in the polymer matrix was investigated systematically. The surface morphologies, structures, luminescence properties, and thermal stabilities of the PMMA composite nanofibers were studied. The effects of the morphologies of the PMMA nanofibers on their luminescence performances were investigated. Finally, the fluorescence recognition performances of the PMMA composite nanofibers were also evaluated. The obtained results should act as a platform for the development of novel luminescent composite polymeric nanofibers containing benzoic acid rare earth complexes and expand their fields of application.

2. Materials and methods

2.1. Materials

The terbium complex $\text{Tb}(4\text{-methylbenzoic acid})_3\text{phen}$ was prepared as reported in the literature [26]. High-molecular-weight PMMA was synthesized through atom-transfer radical polymerization. The number-average molecular weight (\overline{M}_n) of the as-synthesized PMMA was 1.1×10^5 ($\overline{M}_w/\overline{M}_n = 1.12$). The other reagents used were bought from Tianjin Kemiou Chemical Reagent Co., Ltd., and all the solvents used were analytical grade.

2.2. Preparation of electrospinning solutions

The electrospinning solutions used to fabricate smooth luminescent PMMA composite nanofibers were produced as follows: first PMMA (1 g) was dissolved in a solvent mixture of N, N-dimethylformamide and ethyl acetate; the mass percent of PMMA in the solvent mixture was 17%. Then, $\text{Tb}(4\text{-methylbenzoic acid})_3\text{phen}$ was added to this solution in different amounts. Finally, the mixture was stirred continuously for 12 h to obtain uniform electrospinning solutions. The mass percentages of $\text{Tb}(4\text{-methyl benzoic acid})_3\text{phen}$ and PMMA in the resulting solutions were 0.6%, 0.8%, 1%, 6%, 8%, 10%, 12%, 14%, 16%, 18%, and 20%, respectively.

The compositions of the electrospinning solutions used for synthesizing luminescent PMMA composite nanofibers of different morphologies are listed in Table 1. As can be seen from Table 1, equal amounts of PMMA (1 g) were dissolved

Table 1

The compositions of the electrospinning solutions of PMMA fluorescent composite nano-fibers with different morphological structures.

Morphological structures	Solvent	The mass percent of PMMA and solvent (%)	The mass percent of rare earth complex and PMMA (%)
Nano-belt	EA/ethanol	14	1
Porous nano-fiber	Dichloromethane/DMF	14	1
Porous nano-bead	DMF	14	1

in different solvents (ethyl acetate/ethanol, dichloromethane/DMF, and DMF). Next, the appropriate amount of $\text{Tb}(4\text{-methylbenzoic acid})_3\text{phen}$ was added into the solutions. The mixture was stirred overnight, resulting in uniform electrospinning solutions.

2.3. Synthesis of luminescent PMMA composite nanofibers

The as-prepared electrospinning solutions were placed in 15 mL plastic syringes, which had 22G stainless-steel needles attached to them (inner diameter of 0.41 mm). During electrospinning, the solution flow rate was maintained at 0.5 mL/h by using an injection pump. The voltage was maintained at 15 kV. The distance between the tip of the needle and the collecting aluminum plate was 25 cm. The rotational speed of the grounded collecting plate was 100 rpm. The temperature and humidity were kept at 25 °C and 55–85%, respectively. In this manner, luminescent PMMA composite nanofibers with different morphologies could be formed.

2.4. Characterization of synthesized nanofibers

Field-emission scanning electron microscope (FESEM) (Hitachi S4800, Japan) and transmission electron microscope (TEM) (Hitachi H7650) were employed to observe the surface morphologies of the PMMA composite nanofibers. The Fourier transform infrared (FTIR) spectra of samples were collected with a Nicolet NEXUS-670 FTIR spectrometer through KBr disks for wavenumbers of 4000–400 cm^{-1} . The thermal stabilities of the PMMA composite nanofibers were tested with a Netzsch STA 449F3 thermogravimetric analysis (TGA) system. The heating rate was 10 °C/min and the temperatures investigated were 0–800 °C. The luminescence properties of the as-prepared samples were characterized using Gangdong F3800 and Edinburgh FLS 920 fluorescence spectrophotometers.

3. Results and discussion

3.1. Surface morphologies of luminescent PMMA composite nanofibers

Fig. 1 shows FESEM images of the luminescent PMMA composite nanofiber containing $\text{Tb}(4\text{-methyl benzoic acid})_3\text{phen}$ in different amounts. It can be seen from the figure that the average diameter of the as-prepared nanofibers was 100 ± 20 nm. When the $\text{Tb}(4\text{-methylbenzoic acid})_3\text{phen}$ content (mass%) was less than 20%, the surfaces of the as-prepared nanofibers were all smooth. To further investigate the distribution of $\text{Tb}(4\text{-methylbenzoic acid})_3\text{phen}$ in nanofiber, transmission electron microscope (TEM) was employed. Fig. 2 gives the TEM image of the luminescent PMMA composite nanofiber. From Fig. 2, the surfaces of nanofibers are uniformly. There are not the accumulation of rare earth complexes occurred in the nanofibers. This proved that $\text{Tb}(4\text{-methylbenzoic acid})_3\text{phen}$ was uniformly distributed in the PMMA composite nanofibers in large amounts by electrospinning. The results indicated that it should be possible to fabricate luminescent PMMA composite nanofibers that exhibit higher luminescent intensities. This was attributable to two main reasons. First, during electrospinning, the solvent evaporated quickly owing to the high electric field, and the polymer filaments solidified rapidly. Thus, the rare earth complex was dispersed evenly in the nanofibers, as it did not have time to accumulate. Second, the ester groups of the PMMA molecular chain were able to coordinate with the Tb^{3+} ions of the rare earth complex. Fig. 3 shows the FTIR spectrum of a

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