Electrospinning fabrication and properties of Fe$_3$O$_4$/Eu(BA)$_3$phen/PMMA magnetic–photoluminescent bifunctional composite nanoribbons

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ABSTRACT

A new type of magnetic–photoluminescent bifunctional Fe$_3$O$_4$/Eu(BA)$_3$phen/PMMA composite nanoribbons was successfully prepared. The average width of the composite nanoribbons was ca. 19.05 ± 1.83 μm, and the thickness was ca. 786 nm. Fluorescence emission peaks of Eu^{3+} were observed in the Fe$_3$O$_4$/Eu(BA)$_3$phen/PMMA composite nanoribbons. The factors effecting fluorescence intensity were researched via adding different ratios of Eu(BA)$_3$phen to PMMA and Fe$_3$O$_4$ nanoparticles to PMMA. The fluorescent spectra demonstrated that the optimum weight percentage of Eu(BA)$_3$phen to PMMA was 10% due to the concentration quenching effect. Saturation magnetization of the composite nanoribbons was enhanced through introduction of more Fe$_3$O$_4$ nanoparticles, but the fluorescence intensity of the composite nanoribbons was decrease.

1. Introduction

Electrospinning is a fascinating technique to process viscous solutions or melts into continuous fibers with diameters ranging from micrometer to submicron or nanometer. This method not only attracts extensive academic investigations; but also is applied in many areas such as filtration [1], optical and chemical sensors [2], biological scaffolds [3], electrode materials [4] and nanocables [5–7]. Nanoribbon is a kind of nanomaterial of special morphology. It has attracted increasing interests of scientists owing to its anisotropy, large width–thickness ratio, unique optical, electrical and magnetic properties.

Europium complexes have excellent luminescent properties owing to the antenna effect of ligands and the f–f electron transition of Eu^{3+} ions, resulting in important applications in laser [8], phosphor [9], chemosensors and bioimaging probes [10]. However, rare earth complexes usually do not have good thermal and mechanical stabilities and processing properties, which restrict the use of these complexes to promising extensive photophysical applications and practical uses. To overcome these shortcomings, europium complexes must usually be incorporated into organic, inorganic, or organic/inorganic hybrid matrixes, such as zeolites or mesoporous materials, sol–gel silica, or organically modified silicates and polymers [11,12].

Magnetic nanomaterials have attracted a lot of interest of scientists recently owing to their potential applications, such as biomacromolecules separation, catalyst separation, drug/gene delivery and release, and magnetic resonance imaging [13–15].

Magnetic–photoluminescent nanomaterials have been applied in medical diagnostics and optical imaging, etc. At present, some preparations of Fe$_3$O$_4$@RE complex core–shell structure nanoparticles can be found in Refs. [16–18]. However, fabrication of bifunctional magnetic–photoluminescent composite nanoribbons has not been reported in the literatures.

In this paper, we employ electrospinning technique to prepare Fe$_3$O$_4$/Eu(BA)$_3$phen/PMMA composite nanoribbons with magnetic–photoluminescent bifunction. Herein, both the magnetic nanoparticles and luminescent powders are nontoxic. PMMA used as the ribbon template is a kind of stable and biocompatible material. And then we studied the factors effecting fluorescence intensity and saturation magnetization. Some new meaningful results are obtained.

2. Experimental

2.1. Materials

Methylmethacrylate (MMA), benzoylperoxide (BPO), Eu$_2$O$_3$, benzoic acid (BA), phenanthroline (phen), FeCl$_3$·6H$_2$O, FeSO$_4$·7H$_2$O, NH$_4$NO$_3$, polyethyleneglycol (PEG, Mw ≈ 20,000), ammonia, anhydrous ethanol, CHCl$_3$, DMF and deionized water were used. All the reagents are of analytical grade. The purity of Eu$_2$O$_3$ is 99.99%. Deionized water are homemade.

2.2. Preparation of Fe$_3$O$_4$ nanoparticles

Fe$_3$O$_4$ nanoparticles were obtained via a facile coprecipitation synthetic method, and PEG was used as the protective agents to prevent the particles from aggregation. One typical synthetic procedure was as follows: 5.4060 g of FeCl$_3$·6H$_2$O, 2.7800 g of

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$FeSO_4 \cdot 7H_2O$, 4.04 g of NH_4NO_3 and 1.9 g of PEG 20000 were added into 100 ml of deionized water to form uniform solution under vigorous stirring at 50 °C. To prevent the oxidation of Fe^{2+}, the reactive mixture was kept under argon atmosphere. After the mixture had been bubbled with argon for 30 min, 0.1 mol/L of $NH_3 \cdot H_2O$ was added dropwise into the mixture to adjust the pH value above 11. Then the system was continuously bubbled with argon for 20 min at 50 °C, and a black precipitate was formed. The precipitates were collected from the solution by magnetic separation, washed with deionized water for three times, and then dried in an electric vacuum oven for 12 h at 60 °C.

2.3. Synthesis of rare earth organic complexes

Eu(BA)$_3$phen powder was synthesized according to the traditional method as described in Ref. [19]. 0.88 g of Eu_2O_3 was dissolved in 5 ml of concentrated nitric acid and then crystallized by evaporation of excess nitric acid, and $Eu(NO_3)_3 \cdot 6H_2O$ was acquired. $Eu(NO_3)_3$ ethanol solution was prepared by adding 10 ml of anhydrous ethanol into the above $Eu(NO_3)_3 \cdot 6H_2O$. 1.832 g of benzoic acid (BA) and 0.991 g of phenanthroline (phen) were dissolved in 100 ml of ethanol. The $Eu(NO_3)_3$ solution was then added into the solution of BA and phen with magnetic agitation for 3 h at 60 °C. The precipitate was collected by filtration and dried for 12 h at 60 °C.

2.4. Preparation of PMMA

About 100 mL of methylmethacrylate and 0.1 g of benzoylperoxide were mixed in a 250 mL three-necked flask with a backflow device and stirred vigorously at 90–95 °C. Then stopped heating when the viscosity of the mixture solution liked glycerol, and cooled naturally to room temperature. The obtained gelatinous solution was then loaded into test tubes, the influx height was 5–7 cm. After that, the tubes were put in an electric vacuum oven for 48 h at 50 °C, the gelatinous solution was then solidified. At last, the temperature in the oven was raised to 110 °C for 2 h to terminate the reaction.

2.5. Fabrication of magnetic–luminescent composite nanoribbons via electrospinning

In the preparation of precursor solutions, Fe_3O_4 nanoparticles were added in the mixture solution of DMF and $CHCl_3$, then dispersed ultrasonically for 20 min, then PMMA and Eu(BA)$_3$phen were dissolved into the above solution under stirring for 12 h. The dosage of these materials was shown in Table 1.

During the electrospinning process, the precursor solution was loaded into a plastic syringe with a spinneret. A flat iron net was used as a collector and put about 12 cm away from the spinneret, and the spinneret was settled vertically. A positive direct current (DC) voltage of about 6 kV was applied between the spinneret and the collector to generate a stable continuous PMMA-based composite nanoribbon.

2.6. Characterization

The as-prepared Fe_3O_4 nanoparticles and Fe_3O_4/Eu(BA)$_3$phen/PMMA composite nanoribbons were identified by a X-ray powder diffractometer (XRD, Bruker, D8 FOCUS) with Cu Kα radiation. The operation voltage and current were kept at 40 kV and 20 mA, respectively. The morphology and internal structure of Fe_3O_4/Eu(BA)$_3$phen/PMMA composite nanoribbons were observed by a field emission scanning electron microscope (FESEM, XL-30) and a transmission electron microscope (TEM, JEM-2010), respectively. The fluorescent properties of Eu(BA)$_3$phen/PMMA nanoribbons and

Table 1
Compositions of the precursor solutions.

Samples	Compositions				
	Fe$_3$O$_4$ (g)	Eu(BA)$_3$phen (g)	PMMA (g)	DMF (g)	CHCl$_3$ (g)
S1	0.25	0.005	0.5	0.6	9
S2	0.25	0.025	0.5	0.6	9
S3	0.25	0.050	0.5	0.6	9
S4	0.25	0.075	0.5	0.6	9
S5	0.25	0.100	0.5	0.6	9
S6	0.125	0.050	0.5	0.6	9
S7	0.5	0.050	0.5	0.6	9
S8	0	0.050	0.5	0.6	9

Fe_3O_4/Eu(BA)$_3$phen/PMMA composite nanoribbons were investigated by Hitachi Fluorescence spectrophotometer F-7000. Then, the magnetic performance of Fe_3O_4 nanoparticles and Fe_3O_4/Eu(BA)$_3$phen/PMMA composite nanoribbons were measured by a vibrating sample magnetometer (VSM, MPMS SQUID XL).

3. Results and discussion

3.1. Characterizations of the structure and morphology

The phase compositions of the Fe_3O_4 nanoparticles, Eu(BA)$_3$phen complex and composite nanoribbons (S7) were identified by means of XRD analysis, as shown in Fig. 1. It can be seen that XRD pattern of Fe_3O_4 nanoparticles were conformed to the cubic structure of Fe_3O_4 (PDF 74-0748), and no characteristic peaks were observed for other impurities such as Fe_2O_3 and FeO(OH). From the XRD pattern of Eu(BA)$_3$phen complex we can see that the XRD pattern is consisted of no any diffraction peaks, which means the Eu(BA)$_3$phen is an amorphous structure. The XRD analysis result of Fe_3O_4/Eu(BA)$_3$phen/PMMA composite nanoribbons demonstrates that the composite nanoribbons contain Fe_3O_4 nanoparticles.

Fig. 2a illustrates a FESEM image of the as-prepared Fe_3O_4 nanoparticles. The size distribution of the as-prepared nanoparticles was almost uniform, and the diameter of the nanoparticles was 8–10 nm. Fig. 2b and c shows FESEM images of Eu(BA)$_3$phen/PMMA nanoribbons (S8) and Fe_3O_4/Eu(BA)$_3$phen/PMMA composite nanoribbons (S7) respectively. Fig. 3a and b demonstrates the histograms of widths of Eu(BA)$_3$phen/PMMA composite nanoribbons and Fe_3O_4/Eu(BA)$_3$phen/PMMA composite nanoribbons. As revealed in Figs. 2b and 3a, the average width of Eu(BA)$_3$phen/PMMA nanoribbons was 8.56 ± 0.75 μm under the confidence level of 95%, and thickness was about 735 nm. As seen from Figs. 2c and 3b, after
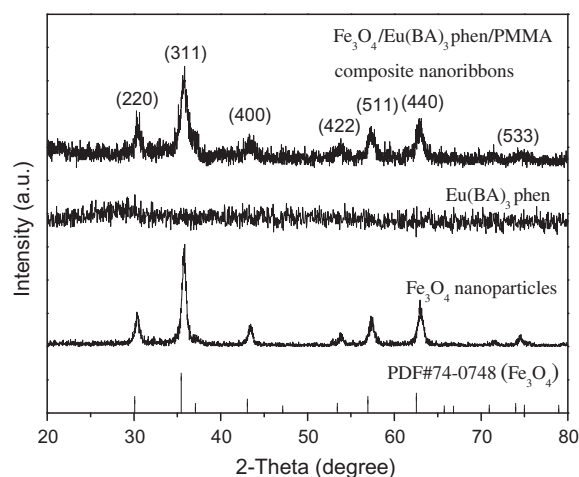

Fig. 1. XRD patterns of Fe_3O_4 nanoparticles, Eu(BA)$_3$phen complex and Fe_3O_4/Eu(BA)$_3$phen/PMMA composite nanoribbons.