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Electricity–magnetism and color-tunable trifunction simultaneously assembled into one strip of flexible microbelt via electrospinning

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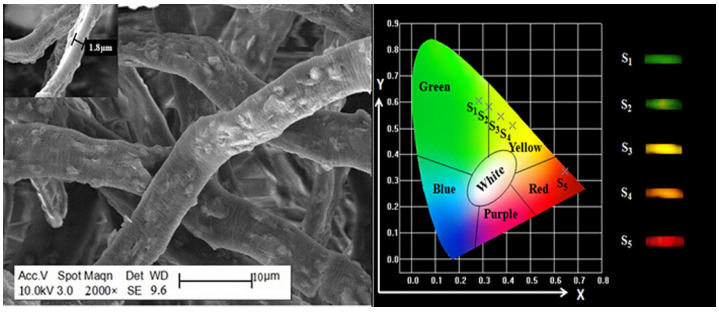
HIGHLIGHTS

- Electricity, magnetism and tunable color were integrated into one strip of microbelt.
- Impact of Fe_3O_4 NPs and PANI on luminescent color was studied for the first time.
- Photoluminescence and fluorescent color of the microbelts can easily be tuned.
- Magnetism and electrical conductance of the microbelts can be tuned.
- Design conception and construction technology are of universal significance.

GRAPHICAL ABSTRACT



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ABSTRACT

For the purpose of developing new-typed multifunctional composite microbelts, novel color-tunable composite microbelts endowed with simultaneously tuned electricity–magnetism performance have been successfully fabricated via facile one-pot electrospinning technology. The obtained trifunctional composite microbelts are composed of polymethyl methacrylate (PMMA) as the matrix, $Tb(BA)_3phen$ and $Eu(BA)_3phen$ (BA = benzoic acid, phen = phenanthroline) complex as luminescence materials, Fe_3O_4 nanoparticles (NPs) as magnetic materials and polyaniline (PANI) as electrically conductive material. Scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), vibrating sample magnetometry (VSM), fluorescence spectroscopy and Hall effect measurement system are used to characterize the morphology, structure and properties of the $[Tb(BA)_3phen + Eu(BA)_3phen]/PANI/Fe_3O_4/PMMA$ composite microbelts. The results indicate that the trifunctional composite microbelts possess excellent fluorescence, saturation magnetization and electrical conduction. The emitting color of the composite microbelts can be tuned by adjusting the mass ratios of $Tb(BA)_3phen$, $Eu(BA)_3phen$, Fe_3O_4 and PANI in a wide color range of red–yellow–green under the excitation of 306-nm single-wavelength ultraviolet light. The electrical conductivity and saturation magnetization of the composite microbelts can be respectively tunable by adding various amounts of PANI and Fe_3O_4 NPs. The trifunctional composite microbelts are expected to possess many potential applications in areas such as full-color display, electromagnetic shielding, molecular electronics, anti-counterfeit materials and biomedicine.

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1. Introduction

Recently, electrospinning, which has been recognized as one of the most convenient, direct and economical methods for the fabrication of polymer microbelts, has aroused much attention of materials scientists all over the world [1–8]. This method not only attracts extensive academic investigations, but is also applied in many areas such as filtration [9], optical and chemical sensors [10], biological scaffolds [11], electrode materials [12] and nanocables [13,14].

Nowadays, some multicolored and color-tunable luminescent materials have been prepared by introducing two or more different luminescent materials [15–17]. Among various luminescent materials, Tb(III) and Eu(III) complexes have excellent luminescent properties owing to the f–f electron transition of Tb^{3+} and Eu^{3+} ions, and they have received a widespread attention due to their excellent performance. Lidia et al. [18] anchored Eu(III) and Tb(III) complexes onto a single SiO_2 transparent layer by sol–gel dip-coating under acidic conditions. This allows high loading of tailored proportions of the red and green emitters within the films and results in highly uniform and easily color-tunable luminescent layers. Lai et al. [19] synthesized color-tunable luminescent materials based on α,ω-diethyl malonate terminated polydimethylsiloxane (EP) and lanthanide ions. The obtained materials exhibited excellent narrow-width red (or green) emissions when incorporating Eu^{3+} (or Tb^{3+}) ions into EP. Moreover, the luminescence spectra of the EP heterometallic complexes were changed via tuning the ratios of Eu^{3+} and Tb^{3+} ions, yielding a wide range of colors.

Polyaniline (PANI), as one of the most important electrically conductive polymers, has been extensively investigated due to its high electrical conductivity, good redox reversibility, processibility, and environmental stability as well as its potential for a variety of applications [20,21]. Submicron-sized belts of pure PANI doped with sulfuric acid or hydrochloric acid have been prepared by electrospinning PANI with suitable molecular weight dissolved in hot sulfuric acid [22], but it remains a great challenge to apply electrospinning to PANI as limited by its molecular weight and solubility. To overcome this problem, most of the researchers electrospun PANI through mixing it with other spinnable polymers [23].

Magnetic Fe_3O_4 nanocrystals have been extensively studied because of their unique and tunable magnetic properties. Their magnetic features have found widespread use in applications as diverse as environmental remediation, magnetic recording, biomacromolecule separation, catalyst separation, drug/gene delivery and release, and magnetic resonance imaging [24–29].

In the last few years, multifunctional composite materials have attracted inevasible attention of scientists all over the world [30]. Ma et al. [4] prepared Fe_3O_4/RE complex (RE = rare earth)/polymer magnetic-fluorescent bifunctional composite nanobelts via electrospinning process. Wang et al. [31] fabricated PANI particles/RE complex/PMMA luminescent-electrical bifunctional composite nanobelts (PMMA = polymethyl methacrylate) via electrospinning. To date, however, research on the electricity–magnetism and color-tunable trifunctional composite microbelts has not been reported in any literatures.

In this paper, we report assembling electricity–magnetism and color-tunable trifunctionality into one [$Tb(BA)_3$phen + $Eu(BA)_3$phen]/PANI/Fe_3O_4/PMMA composite microbelt via one-pot electrospinning technique, and it is expected that trifunctional composite microbelts with excellent luminescence, electrical conduction and magnetic property will be obtained. The morphology, luminescent, electrical and magnetic properties of the flexible composite microbelts were systematically investigated, and some new meaningful results were obtained.

2. Experimental sections

2.1. Materials

Methylmethacrylate (MMA), benzoylperoxide (BPO), Eu_2O_3 (99.99%), benzoic acid (BA), phenanthroline (phen), $CHCl_3$ and dimethylformamide (DMF) were bought from Tianjin Tiantai Fine Chemical Co., Ltd. Terbium oxide (Tb_4O_7, 99.9%) was purchased from Aladdin Chemistry Co. Ltd. Anhydrous ethanol, aniline (ANI), $FeCl_3{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$, NH_4NO_3, polyethyleneglycol (PEG, Mw ≈ 20,000), ammonia and (IS)-(+)-Camphor-10 sulfonic acid (CSA) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ammonium persulfate (APS) was bought from Guangdong Xilong Chemical Co., Ltd. All the reagents were of analytical grade and directly used as received without further purification.

2.2. Synthesis of $Tb(BA)_3$phen and $Eu(BA)_3$phen complexes

$Tb(BA)_3$phen complexes were synthesized according to the traditional method as described in the literature [32]. 0.9346 g of Tb_4O_7 was dissolved in 20 mL of concentrated nitric acid at 60 °C. Then $Tb(NO_3)_3{\cdot}6H_2O$ powders were acquired by evaporation of excess nitric acid and water by heating. $Tb(NO_3)_3$ ethanol solution was prepared by adding 20 mL of anhydrous ethanol into the above $Tb(NO_3)_3{\cdot}6H_2O$. 1.8320 g BA and 0.9910 g of phen were dissolved in 200 mL of ethanol. $Tb(NO_3)_3$ solution was then added into the mixture solution of BA and phen under magnetic stirring for 3 h at 60 °C. The precipitates were collected by filtration and dried for 12 h at 60 °C. The synthetic method of $Eu(BA)_3$phen complexes was similar to the above method, except that the used dosages of Eu_2O_3, BA and phen were 0.1760 g, 0.3664 g and 0.1982 g, respectively.

2.3. Preparation of Fe_3O_4 NPs

Fe_3O_4 NPs were obtained via a facile coprecipitation synthetic method [33], 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 $FeCl_3{\cdot}6H_2O$, 2.7800 g of $FeSO_4{\cdot}7H_2O$, 4.0400 g of NH_4NO_3 and 1.9000 g of PEG 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 dropwise added 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 black precipitates were 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 at 60 °C for 12 h. The obtained Fe_3O_4 NPs were spherical in shape, and the mean size of Fe_3O_4 NPs was ca. 10 nm.

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. When the viscosity of the mixture solution reached up to a certain value just like that of glycerol, the heating was stopped and then natural cooling down 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.