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Parallel spinnerets electrospinning fabrication of novel flexible luminescent–electrical–magnetic trifunctional bistrand-aligned nanobundles

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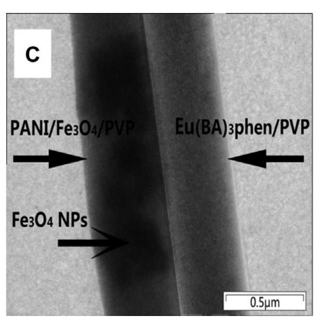
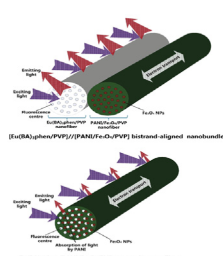
HIGHLIGHTS

- Luminescence–electricity–magnetism bistrand-aligned nanobundle was firstly prepared.
- Nanobundles possess excellent luminescence, electrical conduction and magnetism.
- The nanostructure helps to reduce the impact of PANI and Fe_3O_4 on the fluorescence.
- Luminescence, electrical conduction and magnetism of the nanobundles can be tuned.

GRAPHICAL ABSTRACT

Novel flexible [Eu(BA)$_3$phen/PVP]//[PANI/Fe_3O_4/PVP] luminescent–electrical–magnetic trifunctional bistrand-aligned nanobundles were successfully prepared by specially designed parallel spinnerets electrospinning technology. This peculiar isolated-nanostructure of bistrand-aligned nanobundles can help to realize effective isolating rare earth complex from the dark color PANI and Fe_3O_4 NPs to ultimately reduce the impact of PANI and Fe_3O_4 NPs on fluorescent property of the nanofiber. Meanwhile, high electrical conductivity is achieved owing to consecutive PANI in the nanostructure leading to more effective electrons transport. The bistrand-aligned nanobundles simultaneously possess excellent luminescent performance, electrical conduction and magnetism. The color, luminescent intensity, electrical conductivity and magnetic properties of the bistrand-aligned nanobundles can be tunable by adjusting diversity and content of fluorescent compounds, the content of PANI and Fe_3O_4 NPs, respectively.





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ABSTRACT

Novel flexible luminescent–electrical–magnetic trifunctional bistrand-aligned nanobundles have been successfully fabricated by specially designed parallel spinnerets electrospinning technology. Europium complex Eu(BA)$_3$phen (BA = benzoic acid, phen = 1,10-phenanthroline), polyaniline (PANI) and Fe_3O_4 nanoparticles (NPs) were respectively incorporated into polyvinyl pyrrolidone (PVP) and electrospun into bistrand-aligned nanobundles with Eu(benzoic acid)$_3$(1,10-phenanthroline)/polyvinyl pyrrolidone as one strand nanofiber and polyaniline/Fe_3O_4/polyvinyl pyrrolidone as another strand nanofiber. The morphologies and properties of the final products were investigated in detail by X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), fluorescence spectroscopy, Hall effect measurement system and vibrating sample magnetometry (VSM). It is found that the as-prepared samples exhibit the nanostructures of bistrand-aligned nanobundles. The mean diameter for each individual nanofiber of the bistrand-aligned nanobundles is 350 nm. The obtained trifunctional bistrand-aligned nanobundles possess excellent luminescent performance, electrical conduction and magnetism. Fluorescence emission peaks of Eu^{3+} are observed

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in the bistrand-aligned nanobundles and assigned to the $^5D_0 \rightarrow {}^7F_0$ (581 nm), $^5D_0 \rightarrow {}^7F_1$ (592 nm), $^5D_0 \rightarrow {}^7F_2$ (615 nm) of energy level transitions of Eu^{3+}, and the $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition at 615 nm is the predominant emission peak. The electrical conductivity reaches up to the order of 10^{-3} S/cm. The luminescent intensity, electrical conductivity and magnetic properties of the bistrand-aligned nanobundles can be tunable by adjusting various amounts of rare earth complex, PANI and Fe_3O_4 NPs. The flexible luminescent–electrical–magnetic trifunctional bistrand-aligned nanobundles have potential applications in molecular electronics, microwave absorption and display device owing to their excellent multifunctionality.

1. Introduction

Electrospinning is an outstanding technique to process viscous solutions or melts into continuous fibers with diameters ranging from micrometer to submicron or nanometer. This method has not only attracted extensive academic investigations [1,2], but has also been applied in many areas such as filtration [3], optical and chemical sensors [4], biological scaffolds [5], electrode materials [6], and nanocables [7–10].

In the past few years, multifunctional materials have attracted inevasible attention of scientists all over the world. Up to now, investigation on the luminescent–electrical–magnetic twi- or trifunctional materials has become one of the popular subjects in the field of materials science [11–14]. Electromagnetically functionalized micro/nanostructures of conducting polymers are of special interest due to their potential applications in areas such as electromagnetic interference shielding [15], microwave absorption [16], nonlinear optics [17] and biomedicine [18]. Previously, polyaniline nanotubes containing Fe_3O_4 NPs have been fabricated by an in situ chemical oxidation polymerization in the presence of Fe_3O_4 NPs [19]. Recently, Zhang et al. developed a very simple chemical one-step method to prepare PANI/γ-Fe_2O_3 nanofibers [20,21]. Magnetic–fluorescent nanomaterials have been applied in medical diagnostics and optical imaging, etc. [22,23]. Europium complexes have excellent luminescent properties owing to the antenna effect of ligands and the *f–f* electron transition of Eu^{3+} ions. However, pure rare earth (RE) complexes usually do not have good thermal and mechanical stabilities and processing properties, which restricts 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. At present, some preparations of Fe_3O_4@rare earth (RE) complex core–shell structure nanoparticles have been reported [24–27]. Very recently, preparations of Fe_2O_3/Eu(DBM)$_3$(Bath)/PVP composite nanofibers [28], Fe_3O_4/Eu(BA)$_3$phen/PVP composite nanofibers [29], Fe_3O_4/PVP@Eu(BA)$_3$phen/PVP coaxial nanocables [30], Fe_3O_4/Eu(BA)$_3$phen/PMMA composite nanoribbons [31] and Fe_3O_4/PVP//Eu(BA)$_3$phen/PVP bistrand-aligned composite nanofibers bundles [32] via electrospinning were emerged. PANI particles/rare earth complex/PVP composite nanofibers have also been fabricated via electrospinning process [33,34]. But the electrical conductivity of composite nanofibers only reached 10^{-6} S/cm because PANI particles were not mutually connected in the nanofibers and intervals among PANI particles were existed, resulting in the poor electrical conduction.

It is therefore of considerable interest to develop the luminescent–electrical–magnetic trifunctional nanomaterials which have potential applications in molecular electronics, biomedicine, microwave absorption, electromagnetic shielding, etc. However, according to the previous work, the multifunctional composite nanomaterials suffered low conductivity and heavy losses in fluorescent intensity when PANI and Fe_3O_4 NPs were directly blended with the luminescent compounds. On the basis of the initial studies, if high conductivity is to be achieved, PANI must have good consecutiveness in the nanofibers leading to more effective electrons transport. Meanwhile, in order to achieve strong luminescence, rare earth complex must be effectively isolated from PANI and Fe_3O_4 NPs to ultimately reduce the impact of PANI and Fe_3O_4 NPs on the fluorescent property of the nanobundles. Nanostructure of bistrand-aligned nanobundles can help to realize these academic ideas [35–37]. At the same time, electrospinning is one of the best choices to fabricate this peculiar nanostructure.

In this work, we employ specially designed parallel spinnerets electrospinning technique to prepare flexible [Eu(benzoic acid)$_3$(1,10-phenanthroline)/polyvinyl pyrrolidone]//[polyaniline/Fe_3O_4/polyvinyl pyrrolidone] (denoted as [Eu(BA)$_3$phen/PVP]//[PANI/Fe_3O_4/PVP] for short) luminescent–electrical–magnetic trifunctional bistrand-aligned nanobundles. Of the bistrand-aligned nanobundle, one strand is composed of consecutive PANI, Fe_3O_4 NPs and PVP, and the other one consists of template PVP containing rare earth complex [38]. To the best of our knowledge, no reports on the luminescent–electrical–magnetic trifunctional one-dimensional nanomaterials are found in the references. This nanostructures can successfully help to realize the effective isolation of PANI and Fe_3O_4 NPs from Eu(BA)$_3$phen, thus it is expected that trifunctional bistrand-aligned nanobundles with excellent luminescence, electrical conduction and magnetic properties will be obtained. Herein, the structure, morphology, fluorescence, electrical conduction and magnetic properties of [Eu(BA)$_3$phen/PVP]//[PANI/Fe_3O_4/PVP] flexible trifunctional bistrand-aligned nanobundles were systematically investigated, and some new meaningful results are obtained.

2. Experimental section

2.1. Chemicals

Polyvinyl pyrrolidone (PVP, Mw ≈ 90,000), Eu_2O_3 (99.99%), benzoic acid (BA), phenanthroline (phen) and dimethylformamide (DMF) were bought from Tianjin Tiantai Fine Chemical Co., Ltd. $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, NH_4NO_3, polyethyleneglycol (PEG, Mw ≈ 20,000), ammonia, anhydrous ethanol, aniline and (IS)-(+)-Camphor-10 sulfonic acid (CSA) were bought from Sinopharm Chemical Reagent Co., Ltd. Ammonium persulfate (APS) was purchased 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 europium complexes

Eu(BA)$_3$phen powders were synthesized according to the traditional method as described in Ref. [39]. Eu_2O_3 was dissolved in an amount of concentrated nitric acid and then crystallized via evaporation of excess nitric acid and water by heating, and $Eu(NO_3)_3 \cdot 6H_2O$ was acquired. $Eu(NO_3)_3 \cdot 6H_2O$ ethanol solution was prepared by adding amount of anhydrous ethanol into the above $Eu(NO_3)_3 \cdot 6H_2O$. Benzoic acid (BA) and phenanthroline (phen) were dissolved in ethanol in the molar ratios of