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Flexible Janus nanofiber: A new tactics to realize tunable and enhanced magnetic-luminescent bifunction

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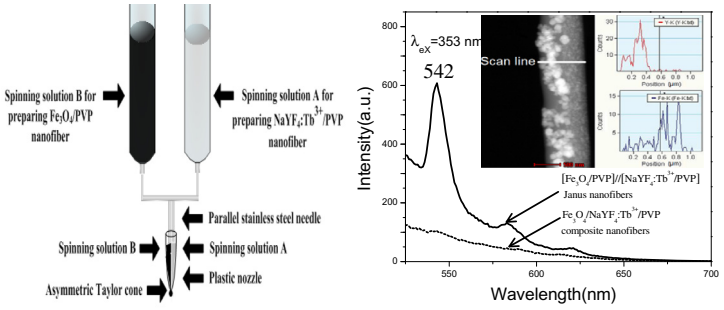
HIGHLIGHTS

- Fe_3O_4/PVP//[$NaYF_4$:Tb^{3+}/PVP] flexible Janus nanofiber was successfully prepared.
- Janus nanofibers provide better performances compared with the composite nanofibers.
- Janus nanofibers simultaneously possess superior magnetic and luminescent properties.
- Magnetism and photoluminescent performances of the Janus nanofibers can be tuned.
- Design conception and construction technology are of universal significance.

GRAPHICAL ABSTRACT

Flexible Janus nanofibers with simultaneous enhanced magnetic-photoluminescent bifunction have been successfully fabricated via electrospinning using a homemade parallel spinneret. Based on the unique feature of the asymmetry dual-sided Janus nanofiber, Fe_3O_4 NPs and $NaYF_4$:Tb^{3+} NPs are isolated in their own domain so that the light absorption of Fe_3O_4 can be weakened, and strong luminescence of the Janus nanofibers can be achieved. Furthermore, the saturation magnetizations and photoluminescent performances of the Janus nanofibers can be tuned by adjusting respective amounts of Fe_3O_4 NPs and $NaYF_4$:Tb^{3+} NPs. The strategy and construction method are of universal significance to fabricate other bifunctional Janus nanofibers.



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ABSTRACT

Magnetic-luminescent bifunctional flexible Janus nanofibers have been successfully fabricated via electrospinning technology using a homemade parallel spinneret. $NaYF_4$:Tb^{3+} and Fe_3O_4 nanoparticles (NPs) were respectively incorporated into polyvinyl pyrrolidone (PVP) and electrospun into Janus nanofibers with $NaYF_4$:Tb^{3+}/PVP as one strand nanofiber and Fe_3O_4/PVP as another strand nanofiber. The morphologies, structures, magnetic and luminescent properties of the as-prepared samples were investigated in detail by X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectrometry (EDS), vibrating sample magnetometry (VSM) and fluorescence spectroscopy. The results show Janus nanofibers simultaneously possess superior magnetic and luminescent properties due to their special structure, and the luminescent characteristics and saturation magnetizations of the Janus nanofibers can be tuned by adding various amounts of $NaYF_4$:Tb^{3+} NPs and Fe_3O_4 NPs. Compared with Fe_3O_4/$NaYF_4$:Tb^{3+}/PVP composite nanofibers, the magnetic-luminescent bifunctional Janus nanofibers provide better performances due to isolating $NaYF_4$:Tb^{3+} NPs from Fe_3O_4 NPs. The novel magnetic-luminescent bifunctional Janus nanofibers have potential applications in the fields of new nano-bio-label materials, drug target delivery materials and

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future nanodevices owing to their excellent magnetic and luminescent performance. More importantly, the design conception and construction technology are of universal significance to fabricate other bifunctional Janus nanofibers.

1. Introduction

In the past few years, nanomaterials have attracted inevasible attention of scientists all over the world [1–3]. Since magnetic-luminescent bifunctional nanomaterials have been applied in medical diagnostics, optical imaging, nanodevice, etc. [4–6], many researches are focused on their preparations and properties in recent years. In general, Fe_3O_4, $MnFe_2O_4$, $CoFe_2O_4$ or $NiFe_2O_4$ is adopted as the magnetic core of the magnetic-luminescent bifunctional nanoparticles (NPs), while quantum dot, rare earth (RE) compound or fluorescent dye is used as the luminescent shell [7–12]. Among these luminescent materials, RE quadrifluoride is one of the high efficient matrixes for RE ion-doped luminescent materials owing to its bumper 4f energy levels and low vibrational energies. Terbium compounds have excellent luminescent properties owing to the f–f electron transition of Tb^{3+} ions, and they have received a widespread attention because of their excellent performance [13,14]. In order to obtain new morphologies of magnetic-luminescent bifunctional nanomaterials, the fabrication of one-dimensional (1D) magnetic-luminescent nanomaterials is an urgent subject of study.

Electrospinning is an outstanding technique to process viscous solutions or melts into continuous fibers or belts with 1D nanostructure [15,16]. This method not only have attracted extensive academic investigations, but is also applied in many areas such as filtration [17], optical and chemical sensors [18,19], biological scaffolds [20,21] electrode materials [22] and nanocables [23,24]. At present, some 1D magnetic-luminescent bifunctional nanomaterials have been prepared via electrospinning [25,26], including Fe_2O_3/$Eu(DBM)_3(Bath)$/PVP composite nanofibers [27], Fe_3O_4/$Eu(BA)_3$phen/PMMA composite nanoribbons [28] and Fe_3O_4/PVP//$Eu(BA)_3$phen/PVP composite nanofibers bundles [29], etc. From these studies, it has been proven that Fe_3O_4 or Fe_2O_3 will greatly decrease the luminescence of RE compounds if they are directly blended with RE compounds. Therefore, luminescent and magnetic materials should be effectively isolated to avoid direct contact if the strong luminescence of the magnetic-luminescent bifunctional nanofibers is achieved. Whilst seeking a way to ultimately reduce the impact of Fe_3O_4 NPs on the fluorescent property of the magnetic-luminescent bifunctional nanofibers, we were inspired by the reports on the Janus nanomaterials [30–34]. 'Janus' is the name of an ancient Roman God, who has two faces peering into the past and the future. Named after this Roman God, Janus particles have two distinguished surfaces/chemistries on the two sides. Pierre-Gilles de Gennes, Nobel Prize in Physics winner, made the Janus particles known to the scientific community. Adopting the unique feature of the asymmetry dual-sided Janus structure, we designed and fabricated magnetic-luminescent bifunctional [Fe_3O_4/PVP]//[$NaYF_4$:Tb^{3+}/PVP] Janus nanofibers with new 1D structure in this paper, and a new kind of spinning spinneret was designed and manufactured to fabricate this novel nanostructure. One strand of the [Fe_3O_4/PVP]//[$NaYF_4$:Tb^{3+}/PVP] Janus nanofiber is composed of template PVP containing Fe_3O_4 NPs (Fe_3O_4/PVP nanofiber), and the other strand consists of PVP containing $NaYF_4$:Tb^{3+} NPs ($NaYF_4$:Tb^{3+}/PVP nanofiber).

To the best of our knowledge, the novel nanostructure of Janus nanofiber with tunable and simultaneous enhanced magnetic-luminescent bifunction has not been reported in literatures. The structure, luminescence and magnetism of the Janus nanofibers were also systematically studied by means of field emission scanning electron microscope (FESEM), X-ray diffractometry (XRD), energy dispersion spectroscopy (EDS), transmission electron microscope (TEM), vibrating sample magnetometer (VSM), fluorescence spectroscopy and UV–vis spectrophotometer.

2. Experimental sections

2.1. Chemicals

Polyvinyl pyrrolidone (PVP, Mw ≈ 30,000), Tb_4O_7 (99.99%), Y_2O_3 (99.99%), N,N-Dimethylformamide (DMF) and trichloromethane ($CHCl_3$) were bought from Tianjin Tiantai Fine Chemical Co., Ltd. $FeCl_3{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$, NH_4NO_3, HNO_3, NaF, polyethyleneglycol (PEG, Mw ≈ 20,000), ammonia, anhydrous ethanol, ethyleneglycol (EG) and oleic acid (OA) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were of analytical grade and directly used as received without further purification. Deionized water was homemade.

2.2. Preparation of oleic acid modified Fe_3O_4 NPs

Fe_3O_4 NPs were obtained via a facile coprecipitation synthetic method, and PEG was used as the protective agent 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 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 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.

To improve the monodispersity, stability and solubility of Fe_3O_4 NPs in the spinning solution, the as-prepared Fe_3O_4 NPs were coated with OA as below: 2.0000 g of the as-prepared Fe_3O_4 NPs were ultrasonically dispersed in 100 ml of deionized water for 20 min. The suspension was heated to 80 °C under argon atmosphere with vigorous mechanical stirring for 30 min, and then 1 ml of OA was slowly added into the above suspension. Reaction was stopped after heating and stirring the mixture for 40 min. The precipitates were collected from the solution by magnetic separation, washed with ethyl alcohol for three times, and then dried in an electric vacuum oven at 60 °C for 6 h.

2.3. Synthesis of $NaYF_4$:Tb^{3+} NPs

Taking $NaYF_4$:5%Tb^{3+} [5% stands for molar percentage of Tb^{3+} to (Y^{3+}+ Tb^{3+})] NPs as an example for the preparation of $NaYF_4$:Tb^{3+} NPs. $NaYF_4$:Tb^{3+} Nps were synthesized via a modified ethyleneglycol refluxing method, and PVP was used as the surfactant. 1.0726 g of Y_2O_3, 0.0935 g of Tb_4O_7 were dissolved in 50 ml of concentrated nitric acid and then crystallized by evaporation of excess nitric acid