Electronic Supplementary Information (ESI)

Neoteric Sandwich-Configurational Composite Film Offering Synchronous Conductive Aeolotropy, Superparamagnetism and

Dual-color Fluorescence

Liu Yang, Wensheng Yu, Jiao Tian, Xue Xi, Dan Li, Xiangting Dong*, Qianli Ma*, Guixia Liu, Jinxian Wang

Key Laboratory of Applied Chemistry and Nanotechnology at Universities of Jilin Province, Changchun University of Science and Technology, Changchun 130022
Fax: 86 0431 85383815; Tel: 86 0431 85582574; E-mail: dongxiangting888@163.com; maqianlimail@163.com

Chemical Reagents

Aniline (ANI), (1S)-(+)-10-camphorsulfonic acid (CSA), CHCl₃, *N*,*N*-dimethylformamide (DMF), methylmethacrylate (MMA), ammonium persulfate (APS), enzoylperoxide (BPO), Eu₂O₃ (99.99 %), Tb₄O₇ (99.99 %) concentrated nitric acid (HNO₃), benzoic acid (BA), 1,10-phenanthroline (phen), oleic acid (OA), ammonia, FeSO₄·7H₂O, FeCl₃·6H₂O, NH₄NO₃, PVP K90 (Mw \approx 1300000), polyethylene glycol (PEG, Mw \approx 20000), PAN, and absolute alcohol were purchased from Beijing Chemical Works. All of the chemicals were analytically pure and directly used as received without further purification. Deionized water was made by ourselves.



Table S1 Electrospinning process, schematic diagrams of four contrastive samples



Table S2 Constituents of the spinnable liquids, homemade spinnerets and electrospinning conditions of four

Electrospinning conditions

contrastive samples

Samples	Constituents of the spinnable liquids	Homemade	Collector	Solidification	Temperature and Relative
		spinnerets		distance	humidity
JNEF/MF/LF	Spinnable liquid I: PANI, PMMA, CHCl3 and DMF	First step: Specially	First step: wire	First step: 16	Temperature:
sandwich-	Spinnable liquid II: Eu(BA) ₃ phen, PMMA, CHCl ₃ and	designed and	netting	cm	20–25 °C
configuration	DMF	assembled Parallel	Second step: wire	Second step:	Relative humidity:
al composite	Spinnable liquid III: Fe₃O₄NPs, PVP and DMF	spinneret	netting	16 cm	18–30%
film	Spinnable liquid IV: Tb(BA) ₃ phen, PAN and DMF	Second step: Single	Third step: wire	Third step:	
		spinneret	netting	16cm	
		Third step: Single			
		spinneret			
CAEF/MF/LF	Spinnable liquid V: PANI, Eu(BA) ₃ phen, PMMA, CHCl ₃	First step: Single	First step:	First step: 14	Temperature:
sandwich-	and DMF	spinneret	revolving drum	cm	20–25 °C
configuration	Spinnable liquid III: Fe₃O₄NPs, PVP and DMF	Second step: Single	Second step: wire	Second step:	Relative humidity:
al composite	Spinnable liquid IV: Tb(BA) ₃ phen, PAN and DMF	spinneret	netting	16 cm	18–30%
film		Third step: Single	Third step: wire	Third step:	
		spinneret	netting	16 cm	
CNEF/MF/LF	Spinnable liquid V: PANI, Eu(BA) ₃ phen, PMMA, CHCl ₃	First step: Single	First step: wire	First step: 16	Temperature:
sandwich-	and DMF	spinneret	netting	cm	20–25 °C
configuration	Spinnable liquid III: Fe ₃ O ₄ NPs, PVP and DMF	Second step: Single	Second step: wire	Second step:	Relative humidity:
al composite	Spinnable liquid IV: Tb(BA) ₃ phen, PAN and DMF	spinneret	netting	16 cm	18–30%
film		Third step: Single	Third step: wire	Third step:	
		spinneret	netting	16 cm	
Two-layer	Spinnable liquid I: PANI, PMMA, CHCl ₃ and DMF	First step: Specially	First step:	First step: 14	Temperature:
composite	Spinnable liquid II: Eu(BA) ₃ phen, PMMA, CHCl ₃ and	designed and	revolving drum	cm	20–25 °C
film	DMF	assembled Parallel	Second step: wire	Second step:	Relative humidity:
	Spinnable liquid VI: Fe ₃ O ₄ NPs, Tb(BA) ₃ phen, PVP, PAN	spinneret	netting	16 cm	18–30%
	and DMF	Second step: Single			
		spinneret			

Characterization Techniques

The as-prepared Fe₃O₄ NPs, the JAEF/MF/LF sandwich-configurational composite film and JAEF/[M-L]F dual-layered composite film were identified *via* using X-ray diffractometer (XRD), which was made by Bruker Corporation with the model of D8 FOCUS and Cu K α radiation, the operation current and voltage were maintained at 20 mA and 40 kV, respectively. The morphology and internal structure of the products were observed by a scanning electron microscope (SEM, JSM-7610F) and optical microscope (OM, CVM500E). An energy dispersive spectrometer (EDS) produced by Oxford Instruments and attached to the SEM was used to analyze elemental compositions. The fluorescence properties of the samples were investigated by using a Hitachi fluorescence spectrophotometer F-7000, and the excitation and emission slits were respectively 1.0 nm and 2.5 nm. The electrical conduction and the magnetization were measured by an ECOPIA HMS-3000 Hall effect measurement system and a vibrating sample magnetometer (VSM, MPMS SQUID XL), respectively.



Fig. S1 (a) SEM images of intersecting surface, (b) superparamagnetic-fluorescent layer, (c) the histogram of diameter distribution of superparamagnetic-fluorescent layer of JAEF/[M-L]F two-layer composite film; SEM image of the first layer of (d) JNEF/MF/LF, (e) CNEF/MF/LF and (f) CAEF/MF/LF sandwich-structured composite film

3.3. Fluorescent Performance

The fluorescent properties of the composite materials are influenced by the doping concentration of fluorescent compound, so it is of great significance to determine the optimal concentration of the fluorescent compound. At the beginning of this study, a series of $Eu(BA)_3phen/PMMA$ composite films doped with various contents of $Eu(BA)_3phen$ were fabricated to research the fluorescent properties and to find the optimal ratio of $Eu(BA)_3phen$ to PMMA for the film. The traditional single-nozzle electrospinning was employed to fabricate $Eu(BA)_3phen/PMMA$ film using spinning solutions L_{II-1} to L_{II-5} respectively. Fig. S2 demonstrates the excitation and emission spectra of $Eu(BA)_3phen/PMMA$ film with different the $Eu(BA)_3phen$ content from 5 % to 25 %. The luminescence intensity increases at first and then decreases with the addition of more $Eu(BA)_3phen$. When the percentage of $Eu(BA)_3phen$ to PMMA is 15 %, the

highest luminescence intensity is obtained. The luminescence intensity decreases as the content of Eu(BA)₃phen exceeds 15 %, which is attributed to too many rare earth complexes introduced into polymer matrix. This behavior may be related to the fluorescence quenching. As illustrated in the excitation spectra (Fig. S2a), a broad excitation band extending from 200 nm to 350 nm with a maximum intensity at 290 nm, which is attributed to the $\pi \rightarrow \pi^*$ electron transition of ligands with a monitoring wavelength of 615 nm. Simultaneously, the characteristic emission peaks (Fig. S2b) of Eu(BA)₃phen are observed under 290-nm UV excitation, which are located at 593 and 615 nm. These peaks are respectively attributed to ${}^5D_0 \rightarrow {}^7F_1$ (593 nm) and ${}^5D_0 \rightarrow {}^7F_2$ (615 nm) energy level transitions of Eu³⁺ ions, and the red light emission at 615 nm assigned to ${}^5D_0 \rightarrow {}^7F_2$ ultra-sensitive transition is primary. The results demonstrate that the nanobelts containing 15 % of Eu(BA)₃phen is adopted for fabricating the nanobelts in the aeolotropic conductive-fluorescent layer of the sandwich-configurational composite film in this study.



Fig. S2 (a) Excitation and (b) emission spectra of Eu(BA)₃phen/PMMA doped with different percentages of Eu(BA)₃phen

The same way is chosen to find the optimum percentage of Tb(BA)₃phen to PAN in the fluorescent layer of the composite film (spinnable liquids L_{IV-1} to L_{IV-5}). The excitation and emission spectra of Tb(BA)₃phen/PAN nanofibers were provided in Fig. S3. From the observation of the excitation spectrum (Fig. S3a), a broad excitation band extending from 200 nm to 350 nm with a strongest peak at 314 nm can be ascribed to $\pi \rightarrow \pi^*$ electron transition of ligands with a monitoring wavelength of 545 nm. Simultaneously, the characteristic emission peaks (Fig. S3b) of Tb(BA)₃phen are observed under 314-nm UV excitation, which are located at 490, 545, 586 and 621 nm. These peaks are respectively attributed to ${}^5D_4 \rightarrow {}^7F_6$ (490 nm), ${}^5D_4 \rightarrow {}^7F_5$ (545 nm), ${}^5D_4 \rightarrow {}^7F_4$ (586 nm), ${}^5D_4 \rightarrow {}^7F_5$ ultra-sensitive transition is dominant. The results imply that the composite nanofiber containing 15 % of Tb(BA)₃phen have the strongest luminescence intensity. Thus, 15 % of Tb(BA)₃phen is adopted for fabricating the nanofibers in the fluorescent layer of the flexible sandwich-configurational composite film in this study.



Fig. S3 (a) Excitation and (b) emission spectra of Tb(BA)₃phen/PAN doped with different percentages of Tb(BA)₃phen

As shown in Fig. S4, the saturation magnetization of the as-prepared Fe_3O_4 NPs is 58.7 emu·g⁻¹ and neither remanence nor coercivity is detected.



Fig. S4 Hysteresis loops of Fe₃O₄ NPs