Supporting Information

Distinctive Sandwich-Type Composite Film and Deuterogenic Three-Dimensional Triwall Tubes Affording Concurrent Aeolotropic Conduction, Magnetism, and Up-/Down-Conversion Luminescence

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Chemicals

Pyrrole (Py), (1S)-(+)−10-camphorsulfonic acid (CSA), CHCl₃, N,N-dimethylformamide (DMF), methacrylate (MMA), ammonium persulfate (APS), enzyolperoxide (BPO), Y₂O₃ (99.99 %), Yb₂O₃ (99.99 %), Er₂O₃ (99.99 %), NH₂F, ethylene glycol, Polyethyleneimine (PEI), concentrated nitric acid (HNO₃), NaOH, FeCl₃·6H₂O, Co(NO₃)₃·6H₂O, KF, KMnO₄, Na₂SO₄, HF, GeO₂, PVP K90 (Mw=1300000), 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 in our own laboratory.

Preparations of Na₂GeF₆:Mn⁴⁺, NaYF₄:Yb³⁺, Er³⁺NPs and CoFe₂O₄ NPs

Na₂GeF₆:Mn⁴⁺ NPs were successfully synthesized by a simple coprecipitation method. Firstly, 1.4204 g of Na₂SO₄ solid powder was dissolved in 20 mL of deionized water, and then 0.4866 g of GeO₂ and 0.0864 g of K₂MnF₆ were fully dissolved in 20 mL of HF (40 wt%) solution. Then, Na₂SO₄ aqueous solution was slowly added into the above-obtained HF solution under magnetic stirring. The sample was centrifuged and washed with ethanol for three times. Finally, the samples
were dried in an oven at 60 °C for 5 h to obtain Na$_2$GeF$_6$:Mn$^{4+}$ NPs$^1$.

NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ NPs were prepared by hydrothermal method$^2$. The detailed preparation process is as follows: 2.25 mmol rare earth oxides RE$_2$O$_3$ (Y$_2$O$_3$, Yb$_2$O$_3$, Er$_2$O$_3$) were put into a 100-mL beaker, in which nY$^{3+}$:nYb$^{3+}$:nEr$^{3+}$=80:18:2 (molar ratio), then dilute HNO$_3$ was added into the beaker. The reaction solution was evaporated by heating and stirring at 120 °C, then cooled down to room temperature to obtain rare earth nitrate. 45 mL ethylene glycol and 0.7568 g of NaNO$_3$ were added into the beaker to acquire the glycol solution of rare earth nitrate by stirring and dissolving, and the solution was named as solution A. 10 mL ethylene glycol solution of PEI with a concentration of 0.005 g·mL$^{-1}$ was put into a 100-mL beaker. NH$_4$F (0.27 mol) and ethylene glycol (30 mL) were added into the mixture, and stirred to dissolve to obtain solution B. The solution A was added into the solution B, and stirred for 10 min. The pH of mixed solution was adjusted to 6-7. Then the mixed solution was transferred to a 100-mL hydrothermal reactor and reacted at 200 °C for 120 min. NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ NPs were obtained by centrifuging and washing the powders with anhydrous ethanol and DMF respectively, and then drying in the vacuum drying oven at 60 °C for 12 h.

CoFe$_2$O$_4$ NPs were prepared by coprecipitation method$^3$. The 0.72 mol NaOH solution was slowly added into the mixed solution of 0.09 mol FeCl$_3$·6H$_2$O and 0.045 mol CO(NO$_3$)$_3$·6H$_2$O, and then the mixture was placed in a water bath, heated to 80 °C and stirred for 2 h. With the addition of NaOH aqueous solution to the above mixed solution, the color of the solution is gradually deepened due to the formation of black precipitates. The black precipitate was collected by magnetic separation, washed it with deionized water and ethanol for three times, and then precipitate was placed in the vacuum drying oven at 60 °C for 12 h to obtain CoFe$_2$O$_4$ NPs.

**Preparation of Spinning Fluids for Fabricating CLJA/MN/LN STCF**

Two different types of spinning fluids were used for preparing the first layer. The spinning fluid A for conductive side of Janus nanobelts was prepared as following. Py, CSA and PMMA were dissolved into the mixed solvent of CHCl$_3$ (13.0000 g) and DMF (1.0000 g) under magnetic stirring (denoted as solution A-a). APS was added into the mixed solvent of CHCl$_3$ (4.5000 g) and DMF (0.5000 g) (named as solution A-b). Solution A-a and solution A-b were placed into an icebox at 0 °C for 20 minutes. Then the solution A-b was added dropwise into the solution A-a in the ice water bath and maintained for 3 h. At last, the obtained mixture was kept at 0 °C for 24 h,
and thus PPy was obtained via the polymerization of pyrrole. For fabricating upconversion luminescent-insulative side of the Janus nanobelts, the spinning fluid B was prepared as following: 1.0000 g of PMMA and NaYF₄:Yb³⁺, Er³⁺ was dissolved into the mixed solvent of CHCl₃ (17.5000 g) and DMF (1.5000 g). The spinning fluid C for making the second layer (magnetic layer) was composed of CoFe₂O₄ NPs, PAN and DMF. The as-prepared CoFe₂O₄ NPs were dispersed into DMF (10.0000 g) under ultrasonic dispersion for 25 min. Then 1 g of PAN was added into the above mixture, and the admixture was heated at 60 °C and stirred until PAN dissolved completely. The spinning fluid D used for fabricating the third layer (luminescent layer) was prepared as following: PVP (1.0000 g) and Na₂GeF₆:Mn⁴⁺ (1.0000 g) were dissolved into the DMF (4.8000 g) under magnetic stirring. The actual compositions of spinning fluids A, B and C were respectively listed in Table S1, S2 and S3.

**Table S1. Compositions of the Spinning Fluid A**

| Spinning fluid A | Py: PMMA (wt %) | Py (g) | CSA (g) | APS (g) | PMMA (g) | DMF (g) | CHCl₃ (g) |
|------------------|----------------|--------|---------|---------|----------|---------|-----------|
| Sₐ₁              | 30%            | 0.3000 | 0.5194  | 0.845   | 1.0000   | 3.0000  | 15.0000   |
| Sₐ₂              | 50%            | 0.5000 | 0.8656  | 1.3862  | 1.0000   | 3.0000  | 15.0000   |
| Sₐ₃              | 70%            | 0.7000 | 1.1216  | 1.8327  | 1.0000   | 3.0000  | 15.0000   |

**Table S2. Compositions of the Spinning Fluid B**

| Spinning fluid B | [NaYF₄:Yb³⁺, Er³⁺]:PMMA (mass ratio) | NaYF₄:Yb³⁺, Er³⁺ (g) | PMMA (g) | DMF (g) | CHCl₃ (g) |
|------------------|--------------------------------------|----------------------|----------|---------|-----------|
| Sₕ₁              | 0.5:1                                | 0.5000               | 1.0000   | 3.0000  | 15.0000   |
| Sₕ₂              | 1:1                                  | 1.0000               | 1.0000   | 3.0000  | 15.0000   |
| Sₕ₃              | 2:1                                  | 2.0000               | 1.0000   | 3.0000  | 15.0000   |

**Table S3. Compositions of the Spinning Fluid C**

| Spinning fluid C | CoFeO₄ : PAN (mass ratio) | CoFeO₄ (g) | PAN (g) | DMF (g) |
|------------------|--------------------------|------------|---------|---------|
| Sₖ₁              | 0.3:1                    | 0.3000     | 1.0000  | 10.0000 |
| Sₖ₂              | 0.5:1                    | 0.5000     | 1.0000  | 10.0000 |
| Sₖ₃              | 1:1                      | 1.0000     | 1.0000  | 10.0000 |

**Preparation of Spinning Fluid for Contrast Samples**

To emphasize the advantages of CLJA/MN/LN STCF, four kinds of contrast samples were
fabricated, including \{[\text{PPy/PMMA}]//[\text{NaYF}_{4}:\text{Yb}^{3+}, \text{Er}^{3+}/\text{PMMA}]\} Janus nanobelt nonarray)\}/[[\text{CoFe}_2\text{O}_4/\text{PAN}]\] nanofiber nonarray)\}/[[\text{Na}_2\text{GeF}_6:\text{Mn}^{4+}/\text{PVP}]\] nanofiber nonarray)\} (named as CLJN/MN/LN) STCF, \{[\text{PPy/NaYF}_{4}:\text{Yb}^{3+}, \text{Er}^{3+}/\text{PMMA}]\] composite nanobelt array)\}/[[\text{CoFe}_2\text{O}_4/\text{PAN}]\] nanofiber nonarray)\}/[[\text{Na}_2\text{GeF}_6:\text{Mn}^{4+}/\text{PVP}]\] nanofiber nonarray)\} (defined as CLCA/MN/LN) STCF, \{[\text{PPy/NaYF}_{4}:\text{Yb}^{3+}, \text{Er}^{3+}/\text{PMMA}]\] composite nanobelt nonarray)\}/[[\text{CoFe}_2\text{O}_4/\text{PAN}]\] nanofiber nonarray)\}/[[\text{Na}_2\text{GeF}_6:\text{Mn}^{4+}/\text{PVP}]\] nanofiber nonarray)\} dual-layered composite film (defined as CLJA/[M-L]N dual-layered composite film). CLJN/MN/LN STCF was fabricated by using spinning fluids S\text{A}_2, S\text{B}_2, S\text{C}_2, and S\text{D}. The spinning fluids for the composite nanobelts array layer of the CLCA/MN/LN STCF and composite nanobelts non-array layer of the CLCN/MN/LN STCF were fabricated by blending spinning fluids S\text{A}_2 and S\text{B}_2 at a volume ratio of 1:1 (named as spinning fluid E), and the other two spinning fluids for second layer and third layer were spinning fluids S\text{C}_2 and S\text{D}. The spinning fluid for magnetic-luminescent layer of CLJA/[M-L]N dual-layered composite film was prepared by mixing equivoluminal spinning fluids S\text{C}_2 and S\text{D} (named as spinning fluid F), and spinning fluids for Janus nanobelts array layer of CLJA/[M-L]N dual-layered composite film were spinning fluids S\text{A}_2 and S\text{B}.

**Table S4.** Electrospinning Process, Schematic Diagrams and Spinning Parameters of the Four Contrast Samples

| Samples       | Electrospinning process                      | Spinning parameters                                                                 |
|---------------|---------------------------------------------|-------------------------------------------------------------------------------------|
| CLJN/MN/LN STCF | ![Schematic Diagram](image-url)              | Spinnerets: specially designed and assembled parallel spinneret, single spinneret    |
|               | ![Schematic Diagram](image-url)              | Collector: rotary drum and wire mesh                                               |
|               | ![Schematic Diagram](image-url)              | Positive direct current voltage:                                                   |
|               | ![Schematic Diagram](image-url)              | 8 kV, 14 kV and 14 kV                                                            |
|               | ![Schematic Diagram](image-url)              | Temperature: 22-25 °C                                                             |
|               | ![Schematic Diagram](image-url)              | Relative humidity: 25 %-30 %                                                       |
Characterization

The as-prepared NaYF₄:Yb³⁺, Er³⁺ NPs, CoFe₂O₄ NPs, Na₂GeF₆:Mn⁴⁺ NPs and CLJA/MN/LN STCF were identified via using an X-ray diffractometer (XRD), which was made by Bruker Corporation with the model of D8 FOCUS and Cu Ka 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 spectroscopy (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 a 980-nm diode laser, and the excitation and emission slits were respectively set to 2.5 nm and 2.5 nm. The electrical conductance and the magnetization were measured by an ECOPIA HMS-3000 Hall effect measurement system and a vibrating sample
magnetometer (VSM, MPMS SQUID XL), respectively.

**Appearance and Structure**

The SEM image of the prepared NaYF₄:Yb³⁺, Er³⁺ NPs and the diameter distribution histogram of particles are respectively shown in Figure S1a and Figure S1c. The diameter of spherical NaYF₄:Yb³⁺, Er³⁺ NPs is 139.13 ± 0.18 nm. The SEM image of the prepared Na₂GeF₆:Mn⁴⁺ NPs and the diameter distribution histogram of particles are indicated in Figure S1b and Figure S1d, respectively. The diameter of Na₂GeF₆:Mn⁴⁺ NPs is 248.21±3.1 nm.

**Figure S1.** (a, b) SEM images and (c, d) histograms of particle diameter distribution of (a, c) NaYF₄:Yb³⁺, Er³⁺ NPs and (b, d) Na₂GeF₆:Mn⁴⁺ NPs

**Figure S2.** SEM images of the first layer of CLCA/MN/LN STCF (a), CLCN/MN/LN STCF (b), CLJN/MN/LN STCF (c) and magnetic-luminescent layer of CLJA/[M-L]N dual-layered composite film (d); Histograms of width distribution of nanobelts in CLCA/MN/LN STCF (e), CLCN/MN/LN STCF (f), CLJN/MN/LN STCF (g) and diameter distribution of nanofibers in (h) magnetic-luminescent layer of CLJA/[M-L]N dual-layered composite film

**References**

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