

# External Current Controlled Dynamic Display by Integrating Upconversion Nanoparticles with Power Density Dependent Color into NIR Luminescent Diodes

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## 1. Experimental Procedures

### Materials

Yttrium(III) oxide ( $Y_2O_3$ ), ytterbium (III) oxide ( $Yb_2O_3$ ), erbium (III) oxide ( $Er_2O_3$ ), trifluoroacetic acid ( $CF_3COOH$ ), sodium trifluoroacetate ( $CF_3COONa$ ), oleic acid (>90%), oleylamine (C18:80-90%) and 1-octadecene (>90%). LEDs chip with rated voltage of 3V.

### Preparation of RE ( $CF_3COO$ )<sub>3</sub> (RE=Y, Yb, Er)

Typically, a theoretical amount of  $RE_2O_3$  was added to a solution of 50% aqueous trifluoroacetic acid, then the mixture was heated to 80 °C and maintaining for several hours until the mixture changed clear then evaporate the water and acid left at 120 °C. The solid product was dried under vacuum at 60 °C for several hours and then dissolved in deionized water to provide 0.2 M  $RE(CF_3COO)_3$ .

### Preparation of $\alpha$ -NaYbF<sub>4</sub>:Er<sup>3+</sup>(2%) core

Typically, 1.0 mmol of RE ( $CF_3COO$ )<sub>3</sub> (RE = Yb:Er) with ratio of 98:2, precursor and sodium trifluoroacetate (2.0mmol) were added together to the solvent containing oleic acid (8 mL) and 1-octadecene (12 mL). The mixture was heated to 150 °C and maintaining for 40 min with stirring to remove the most of water and then cooled down to room temperature naturally under stirring. Then, 8 mL of oleylamine (OM) was added to the solution. The mixture was heated to 120°C under vacuum to remove the water and oxygen left in the solution. Then the solution was heated up to 330 °C under the nitrogen atmosphere and kept for 30 min. After that, the solution was cooled down to room temperature under stirring. The  $\alpha$ -NaYbF<sub>4</sub>: Er nanoparticle were collected by addition of ethanol and centrifugation at 7000 rpm for 6 min. To avoid loss of the cubic core product, the nanoparticles were washed one time and diffused in 10 mL cyclohexane.

### **Preparation of $\beta$ -NaYbF<sub>4</sub>:Er<sup>3+</sup>(2%) core**

To convert the  $\alpha$ -NaYbF<sub>4</sub>:Er<sup>3+</sup> to the hexagonal phase, sodium trifluoroacetate (1.0mmol) was added to the solution containing oleic acid (10 mL) and 1-octadecene (10 mL). The mixture was heated to 150 °C and maintaining for 30 min with stirring to remove the water and then cooled down to room temperature, 5mL of the hexane solution containing 0.5 mmol cubic core was added to a mixture and residual water and oxygen was again removed by degassing at 120°C for 30min under N<sub>2</sub>. The resulting solution was then heated to 330°C and kept for 30 minutes before naturally cooling down to room temperature. Excess ethanol will then be added to precipitate the nanocrystals followed by centrifugation at 7000 rpm for 6 min. The collected  $\beta$ -NaYbF<sub>4</sub>:Er<sup>3+</sup> crystals will then be dispersed in 10 mL hexane.

### **Preparation of $\beta$ -NaYbF<sub>4</sub>:Er<sup>3+</sup>(2%)@NaYF<sub>4</sub> core-shell**

To get the structure of core-shell nanoparticles, Na(CF<sub>3</sub>COO) (0.5 mmol) and Y(CF<sub>3</sub>COO)<sub>3</sub> (0.5 mmol) was first added to the solution of 10 mL oleic acid and 10 mL 1-octadecene and heated to 150 °C to get a clear solution, then the  $\beta$ -NaYbF<sub>4</sub>:Er(2%) core (0.5 mmol) were added into above mixture. The mixture was heated to 100 °C to remove hexane, and then heated to 120°C under vacuum to remove the water and oxygen left in the solution. Then solution was heated up to 330 °C with the nitrogen atmosphere and kept for 30 min before naturally cooling down to room temperature. The final product was collected by adding 10 mL of ethanol to precipitate the nanocrystals and centrifuged at 7000 rpm for 6 min. The nanoparticles were washed several times and then stored in 10 mL cyclohexane.

### **Preparation of maple leaf and tulip shaped PDMS films with UC materials**

To prepare composite PDMS film, the mixture of the PDMS pre-polymer and the curing agent and the dispersion of cyclohexane containing UCNPs with the ratio of 5:1:5 (v/v/v) were deposited dropwise onto a glass substrate (2.5 cm\*2.5 cm). The substrate was heated at 50°C for 30 min to volatile low boiling point solvent. Then the mixture was heated at 100°C for an hour to cure the PDMS. After curing, polymerized film was detached from the glass carefully. Then the film was put into the puncher with maple leaf shape to get patterned composite film.

### **Measurement of upconversion absolute quantum yield**

Fluorescence spectroscopy (Edinburgh LFS920) was modified by using Ocean Optics UV-VIS-NIR CCD (QE65000) as a detector to collect the 980 nm light and the UC emissions. An integrating sphere was also used to measure the efficiency data. The response of the detection systems in photon flux was determined using a calibrated VIS-NIR lamp (Ocean Optics LS-1 1-CAL). The quantum yield of UC emission of the nanoparticles was calculated with the following equation.

$$QY = E_{\text{sample}} / (A_{\text{blank}} - A_{\text{sample}})$$

Where QY is the quantum yield,  $E_{\text{sample}}$  is the photons emitted per unit time of the sample in the UC emission range,  $A_{\text{blank}}$  and  $A_{\text{sample}}$  are the photons emitted per unit time by the excitation light in the absence and presence of the UCNPs samples, respectively.

### **Fabrication of LEDs array with UC materials coated on the surface of NIR chip.**

To fabricate the LEDs with power density sensitive UCNPs and UCNPs with green emission only, solution of UCNPs firstly vacuumed drying to get solid powder, and commercial A B silica gel for

LEDs were mixed with the ratio of 4:1(m/m), then amount of UCNPs powders were added to the mixture to form the fixed material with mass ratio of 1:5. The LED bulbs with tunable color upon tailoring the external current were fabricated by depositing above prepared mixture on the surface of NIR chip. Meanwhile, UCNPs powders with only green emission were integrated with NIR-LED with the same step with the sensitive ones. Finally, we designed printed-circuit-board (PCB) with different control lines to form the different patterns with different intensity of current.

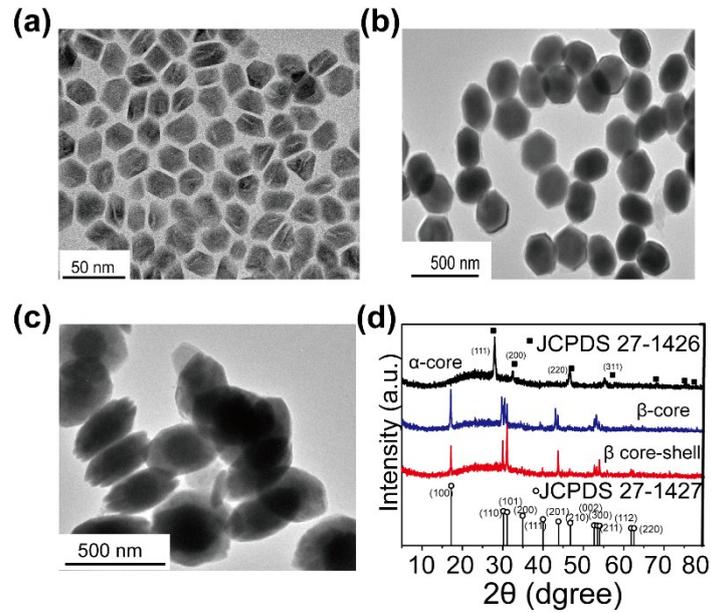
#### **Measurement of the brightness of NIR-LED fabricated by UC materials**

The brightness of the LED was measured with CS200 (KONICA MINOLTA), Setting the brightening voltage as 1 V, and the range of the voltage changed from 1 to 3V, recording different brightness of the LED and corresponding current.

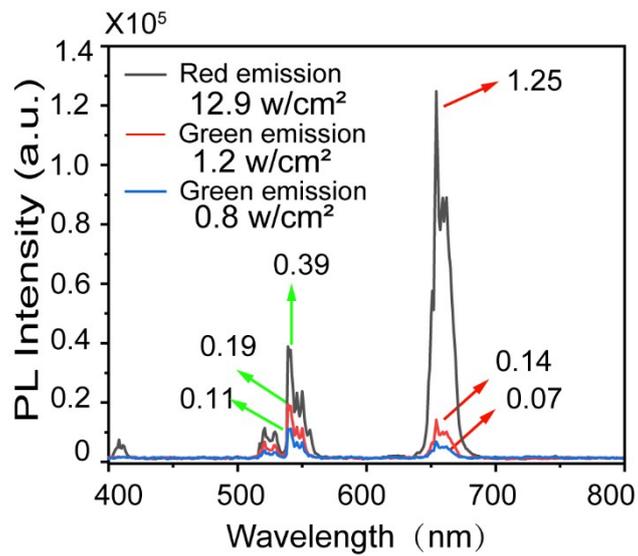
#### **Characterization**

Information of particle size and morphology Transmission electron microscopy (TEM, Tecnai G220 S-TWin) were obtained at an acceleration voltage of 200 kV, EDX spectrum elemental mapping and line-scan were recorded at 300 kV. Powder X-ray diffraction (XRD) measurements were carried out on a Rigaku D/MAX-2400 diffractometer with Cu-K $\alpha$  radiation (40 kV, 40 mA,  $\lambda=1.54184 \text{ \AA}$ ). The absorption spectra of the Powder were measured using a Hitachi U-4100 spectrophotometer. Upconversion luminescence spectra were measured with an Edinburgh FS5 fluorescence spectrometer under the excitation of an external 0–2 W adjustable 980 nm CW laser (Changchun New Industries Optoelectronics Technology Co., Ltd, China), using RXN-605D Variable 60V 5A DC Power Supply (AC 220V $\pm$ 10% 50Hz) for the LEDs, the brightness of the LED was measured with CS200 (KONICA MINOLTA). all the digital images were taken by iPhone.

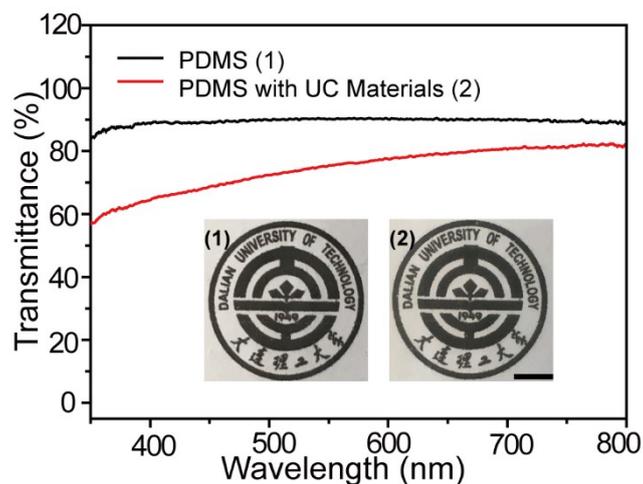
## **2. Supporting Figures**



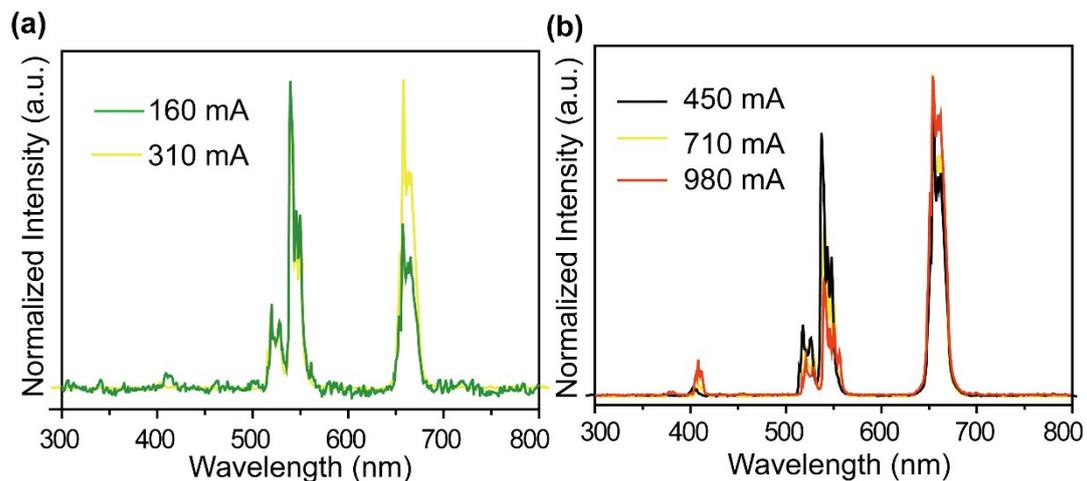
**Fig. S1.** (a-c) TEM images of  $\alpha$ -NaYbF<sub>4</sub>: Er<sup>3+</sup> (2%),  $\beta$ -NaYbF<sub>4</sub>: Er<sup>3+</sup> and  $\beta$ -NaYbF<sub>4</sub>: Er<sup>3+</sup>@NaYF<sub>4</sub> nanoparticles and their XRD patterns, d.



**Fig. S2** Luminescence spectra of red emission and green emission of prepared micro-disk in the solution of cyclohexane.



**Fig. S3** Transmittance spectra of PDMS (blank line) and composite films with UC Materials, the inset is the digital image of pure PDMS film and PDMS film with UC Materials.



**Fig. S4** Normalized luminescence spectra of LED fabricated with UCNPs at different intensity of current with the voltage of 3V.

**Table S1** Brightness of the NIR luminescent diodes integrated with UC materials

|                        |     |     |     |     |     |      |
|------------------------|-----|-----|-----|-----|-----|------|
| I (mA)                 | 72  | 270 | 500 | 728 | 940 | 1050 |
| L (cd/m <sup>2</sup> ) | 4.5 | 46  | 156 | 279 | 400 | 440  |