

**Chiral Electronic Transitions of  $\text{YVO}_4:\text{Eu}^{3+}$  Nanoparticles  
in Cellulose based Photonic Materials with Circularly  
Polarized Excitation**

Guang Chu<sup>a</sup>, Xuesi Wang<sup>b</sup>, Tianrui Chen<sup>a</sup>, Wen Xu<sup>b</sup>, Yu Wang<sup>\*a</sup>, Hongwei Song<sup>b</sup> and  
Yan Xu<sup>\*a</sup>

a) State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China

b) State Key Laboratory of Integrated optoelectronics, Jilin University, 2699 Qianjin Street, Changchun 130012, China;

## Supporting Information

### Experimental Section

#### Preparation of cellulose nanocrystals (CNCs)

In a typical experiment, 50 g of bleached commercial cotton pulp was milled using a commercial pulper containing 1000 mL of deionized water, followed by oven-drying. Next, 20 g milled pulp was hydrolysed in 200 mL of H<sub>2</sub>SO<sub>4</sub> (1g pulp / 10 ml H<sub>2</sub>SO<sub>4</sub>) aqueous solution (64 wt.%) under vigorous stirring at 45 °C for 60 min. The pulp slurry was diluted with cold deionized water (about ten times the volume of the acid solution used) to stop the hydrolysis, and allowed to subside overnight. The clear top layer was decanted and the remaining cloudy layer was centrifuged. The supernatant was decanted and the resulting thick white slurry was washed three times with deionized water. Finally, the white thick suspension was placed into a Millipore ultrafiltration cell (model 8400) to wash the cellulose with deionized water until the pH of solution was stable at 2.4. The thick pulp slurry from the Millipore cell was diluted to desired concentration with constant stirring<sup>1</sup>.

CNCs alkaline solution was prepared by titration of the above acidic CNCs aqueous suspension with the appropriate amount of 0.1 M NaOH (aq) to reach alkalinity. Base was added slowly with constant stirring and the progress was monitored with a pH meter until 10.7 was reached. The amount of base used was depended on the degree of sulfonation of CNCs. This procedure can be repeated with several different CNCs batches and shows a good reproducibility<sup>2</sup>.

Ultrasound treatment has been used to increase the chiral nematic pitch in solution and red-shift the reflection wavelength of CNCs films. Samples of CNCs alkaline suspension were sonicated using a Sonics Vibra-Cell (VCX-750, Sonics & Materials, Inc). Typically, 50 mL of 3.5 wt% CNCs alkaline suspension was placed in a 100 mL glass beaker and sonicated at 50% (for suspension of CNC-2) or 100% (for suspension of CNC-3) of the maximum power for 5 min. The suspension of CNC-1 was prepared under static conditions<sup>3</sup>.

#### Preparation of YVO<sub>4</sub>:Eu<sup>3+</sup> (2 mol%) nanoparticles (NPs)

The synthesis of YVO<sub>4</sub>:Eu<sup>3+</sup> NPs was similar to the previous reports<sup>4</sup>. The whole process was carried out at 60 °C. A 0.1 M solution of (Y, Eu)(NO<sub>3</sub>)<sub>3</sub> (30 mL and 3 mmol, Y<sup>3+</sup>:Eu<sup>3+</sup>=49:1) was mixed with a 0.1 M solution of sodium citrate (22.5 mL and 2.25 mmol). Then a white precipitate of lanthanide citrate was formed, which was completely dissolved by the addition of a 0.1 M solution of Na<sub>3</sub>VO<sub>4</sub> (22.5 mL and 2.25 mmol). The reaction solution turned to clear and colorless and subsequently aged at 60 °C for 30 min, forming the final YVO<sub>4</sub>:Eu<sup>3+</sup> NPs. The resulting YVO<sub>4</sub>:Eu<sup>3+</sup> NPs were washed with ethanol and separated by centrifugation. Finally, the prepared YVO<sub>4</sub>:Eu<sup>3+</sup> NPs were dispersed in water. In order to remove the excess ions, the solution was dialyzed against water (molecular weight cutoff of 8000-14000 Da) for 3 days until the pH was stable at 7.6. The solution of YVO<sub>4</sub>:Eu<sup>3+</sup> NPs were concentrated by eliminating water with rotary evaporator under mild conditions (40

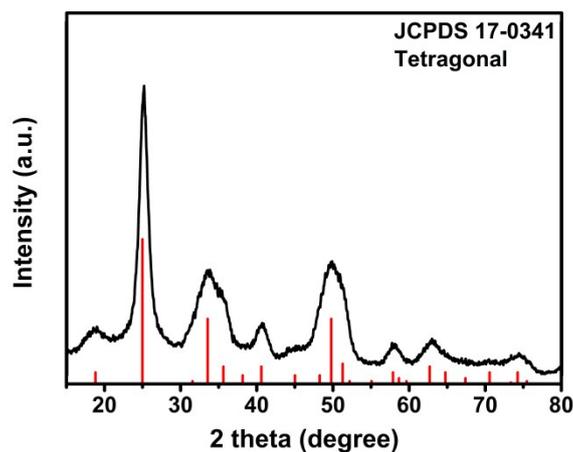
°C under vacuum), and then dilute with water to 75 ml. The concentration of the final colloidal solution is about 0.03 M.

## Supporting Figures and Tables

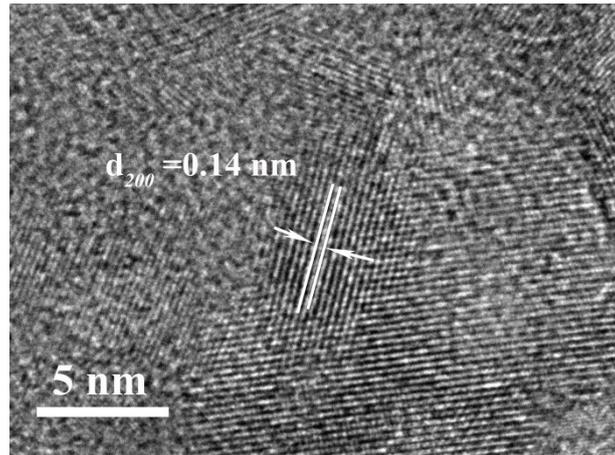
**Table S1.** Preparation of CNCs/YVO<sub>4</sub>:Eu<sup>3+</sup> NPs (CY) composite films.

Composite film	Volume of CNCs-1 suspension (ml)	Volume of NPs solution (ml)
CY1a	5	0
CY1b	5	0.5
CY1c	5	1
CY1d	5	2
CY1e	5	3
CY1f	5	4

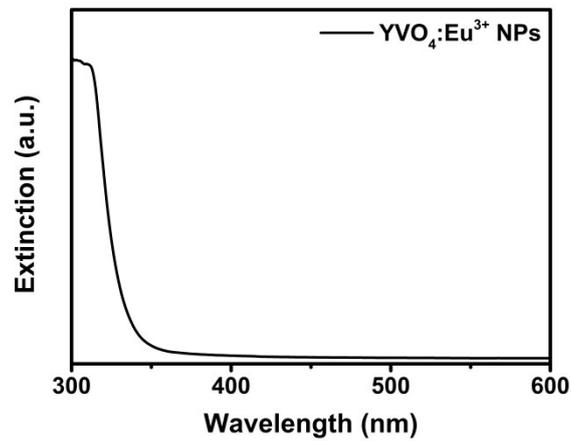
The concentration of the CNCs suspension and the YVO<sub>4</sub>:Eu<sup>3+</sup> NPs solution are 3.5 wt% and 0.03 M, respectively. The composite films prepared by CNCs-2 suspension and CNCs-3 suspension are designated as CY2a-f and CY3a-f, respectively.



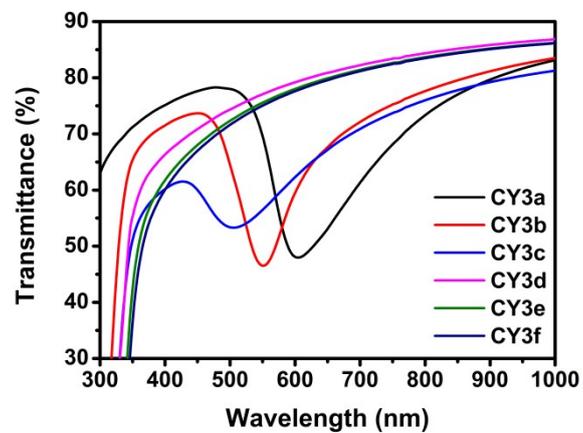
**Fig. S1.** XRD patterns of YVO<sub>4</sub>:Eu<sup>3+</sup> NPs, showing the tetragonal structure of the NPs.



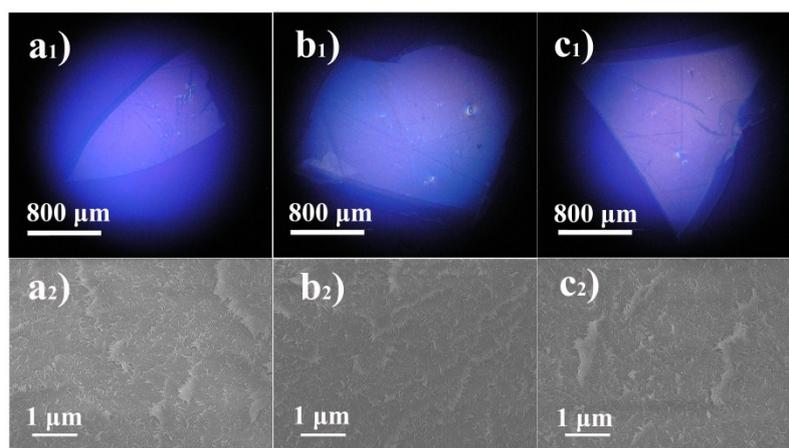
**Fig. S2.** HRTEM image of  $\text{YVO}_4:\text{Eu}^{3+}$  NPs, showing the presence of crystalline domains of  $\text{YVO}_4$  with the average  $d_{200}$ -spacing of the lattice fringes around 0.14 nm.



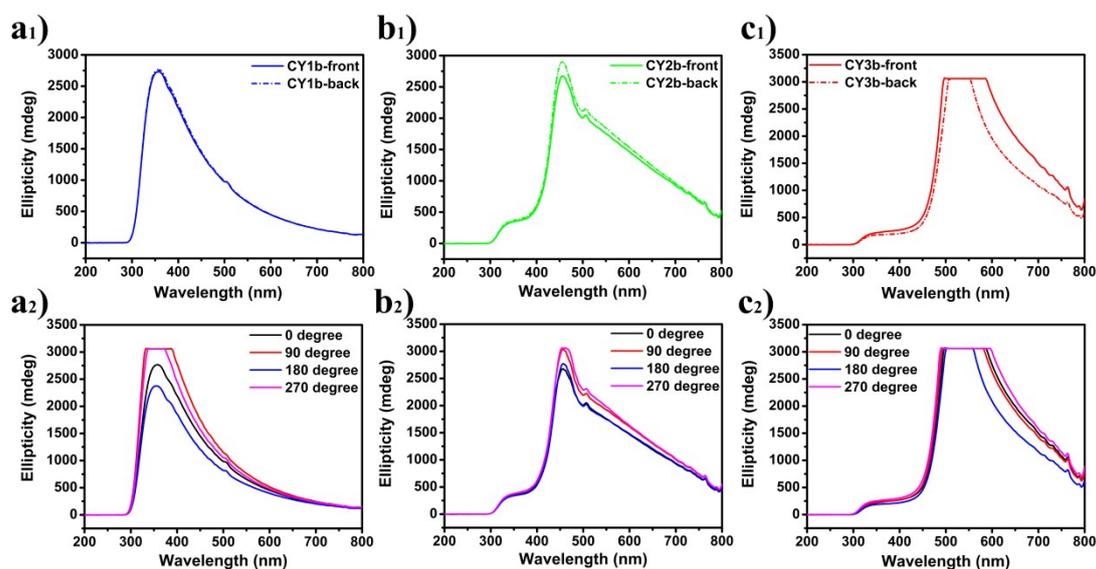
**Fig. S3.** UV spectra of the water suspension of  $\text{YVO}_4:\text{Eu}^{3+}$  NPs.



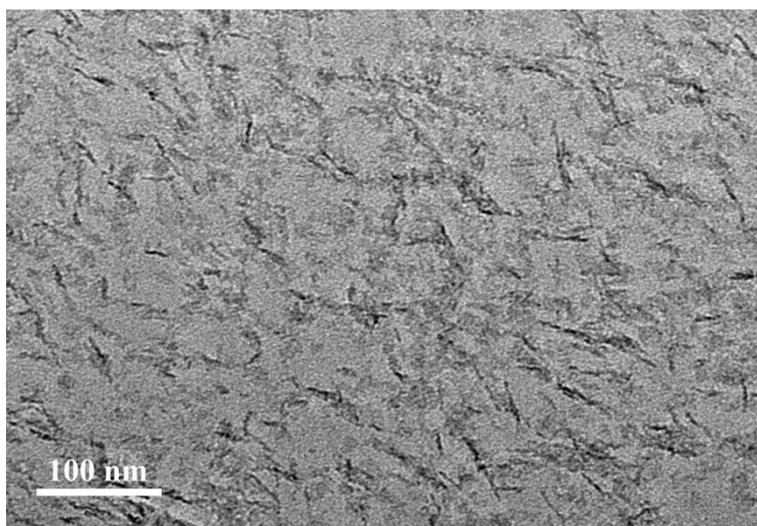
**Fig. S4.** UV-Vis spectra of the CY films with varying amount of  $\text{YVO}_4:\text{Eu}^{3+}$  NPs.



**Fig. S5.** POM and SEM images of the CY films with excess amount of  $\text{YVO}_4:\text{Eu}^{3+}$  NPs, showing complete disappearance of birefringence and periodic structure. ( $\mathbf{a}_1\text{-c}_1$ ) are the POM images of CY3d-f and ( $\mathbf{a}_2\text{-c}_2$ ) are the corresponding SEM images.



**Fig. S6.** The “front-and-back” CD measurements of the sample of CY1b, CY2b and CY3b, respectively, are presented in ( $\mathbf{a}_1$ )-( $\mathbf{c}_1$ ). And ( $\mathbf{a}_2$ )-( $\mathbf{c}_2$ ) is the CD spectra of CY1b, CY2b, and CY3b rotated at different angles normal to the beam path.



**Fig. S7.** TEM image of the mixed suspension of YVO<sub>4</sub>:Eu<sup>3+</sup> NPs doped with CNCs on dry state, which shows a linear arrangement of the NPs, confirming the interaction between CNCs and YVO<sub>4</sub>:Eu<sup>3+</sup> NPs.

**Table S2.** The quantum efficiency of CY1b, CY2b, CY3b and the corresponding YVO<sub>4</sub>:Eu<sup>3+</sup> NPs ( $\lambda_{\text{ex}}=300$  nm).

Sample	CY1b	CY2b	CY3b	YVO <sub>4</sub> :Eu <sup>3+</sup> NPs
<b>Quantum Efficiency</b>	2.40%	3.00%	3.80%	2.60%

**Table S3.** The fluorescence lifetime for CY1b, CY2b, CY3b and the corresponding YVO<sub>4</sub>:Eu<sup>3+</sup> NPs recording at 464 nm.

Sample	Decay Time (t)	
	$\tau_1/\text{ms}$	$\tau_2/\text{ms}$
CY1b	0.69	0.19
CY2b	0.89	0.33
CY3b	0.72	0.13
YVO <sub>4</sub> :Eu <sup>3+</sup> NPs	0.85	0.4

**Reference:**

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