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Chiral Nematic Mesoporous Films of $ZrO_2:Eu^{3+}$: New Luminescent Materials

Guang Chu,[a] Jing Feng,[b] Yu Wang[*a], Xiao Zhang,[c] Yan Xu[*a] and Hongjie Zhang[b]

Preparation of nanocrystaline cellulose (NCC)

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, the milled pulp was hydrolysed in 200 mL of H_2SO_4 (1g pulp / 10 ml H_2SO_4) aqueous solution (64 wt.%) under vigorous stirring at 45 ºC 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. The thick pulp slurry from the Millipore cell was dispersed by subjecting it to ultrasound treatment for 5 min, subsequently diluted to desired concentration.[1]

Preparation of chiral nematic mesoporous silica films (CNMS)

To prepare the CNMS films, tetramethoxysilane (TMOS) was added to NCC aqueous suspension (3.5 wt.%) with a ratio of (0.94ml TMOS / 20ml to 3.5% NCC (4g TMOS/3g NCC). The mixture was poured into polystyrene Petri dishes (5 mL/55 mm Petri dish) after stirring for 90 min at atmospheric temperature, followed by evaporation under ambient conditions to give rise to a free-standing cellulose/silica composite films. The CNMS films were obtained by calcining the cellulose/silica composite films at 540 °C for 6 h in a muffle furnace at a heating rate of 2 °C/min. The CNMS films which give a strong green color are designated as CNMS-S. CNMS-L were prepared under the same condition with the ratio of 7g TMOS/3g NCCs and it gives a red color.[2]

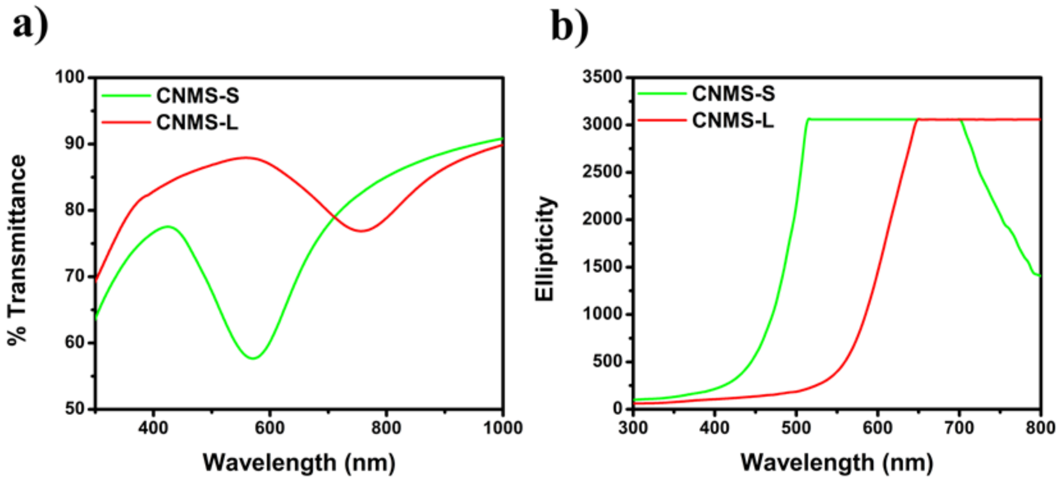

Fig. S1. (a) UV-Vis spectra of the CNMS-S and CNMS-L films showing the photonic band gap in both materials. (b) CD spectra of the CNMS-S and CNMS-L films. The spectra appear cut off since the peak are greater than the maximum detectable signal on the spectropolarimeter that was used.

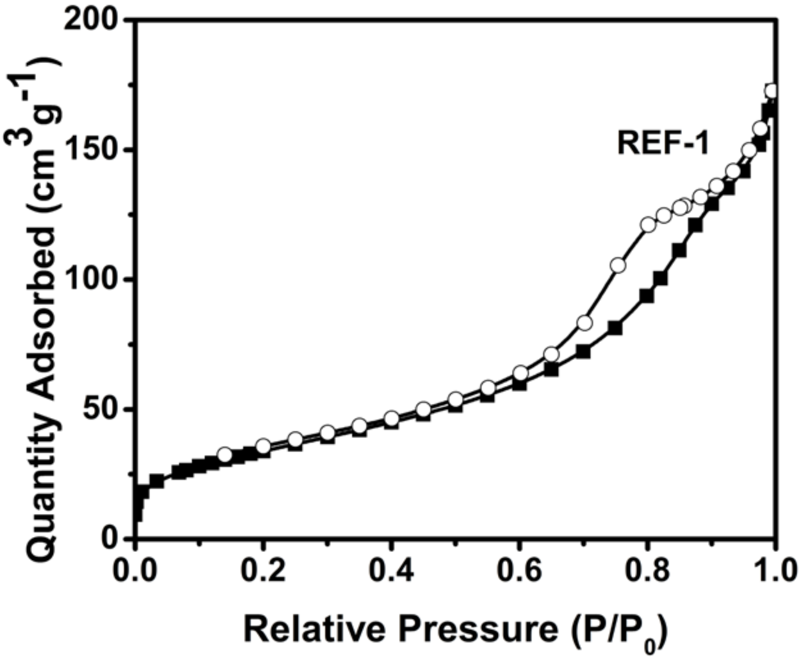

Fig. S2. Nitrogen adsorption-desorption isotherm of REF-1.

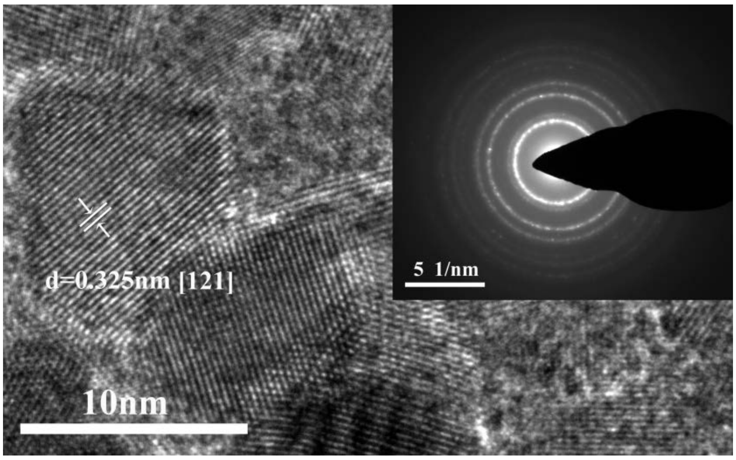

Fig. S3. HRTEM image of EDCNMZ-1 showing the presence of crystalline domains of ZrO_2 with the average d_{121}-spacing of the lattice fringes around 0.325 nm; Inset is the SEAD of EDCNMZ-1.

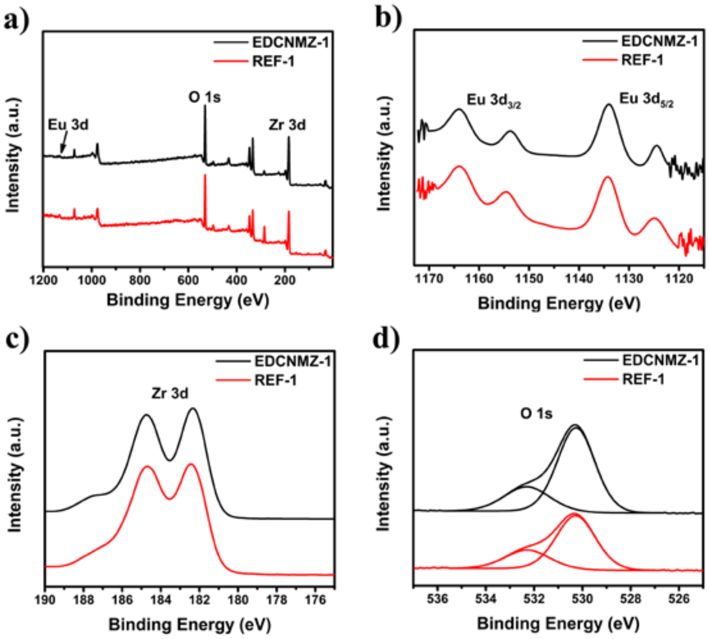

Fig. S4. (**a**) XPS survey spectra of EDCNMZ-1 and REF-1. (**b**) Deconvoluted XPS peaks of Eu3d. (**c**) Deconvoluted XPS peaks of Zr3d. (**d**) Deconvoluted XPS peaks of O1s.

Table S1. The photoluminescent lifetime of EDCNMZ-1 and REF-1 as a function of emission wavelength.

Sample	Decay time (t) λ_{em}=591nm		Decay time (t) λ_{em}=605nm		Decay time (t) λ_{em}=596nm		Decay time (t) λ_{em}=613nm	
	τ_1/ms	τ_2/ms	τ_1/ms	τ_2/ms	τ_1/ms	τ_2/ms	τ_1/ms	τ_2/ms
EDCNMZ-1	4.97	0.49	5.24	0.43	2.68	0.21	2.04	0.27
REF-1	3.55	0.22	4.37	0.22	1.69	0.19	1.91	0.21

1. S. Beck-Candanedo, D. Viet and D. G. Gray, *Langmuir*, 2006, 22, 8690-8695.
2. K. E. Shopsowitz, H. Qi, W. Y. Hamad and M. J. Maclachlan, *Nature*, 2010, 468, 422-425.