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Chiral nematic mesoporous films of Y_2O_3:Eu^{3+} with tunable optical properties and modulated photoluminescence

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Experimental procedures.

Preparation of nanocrystalline 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, 20 g of 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 ˚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 dispersed by subjecting it to ultrasound treatment for 5 min, subsequently diluted to desired concentration.[1]

Fabrication of chiral nematic mesoporous silica films (CNMS).

To prepare the CNMS films, tetramethoxysilane (TMOS) was added to NCC aqueous suspension (3.5 wt.%) with different ratio of NCC / TMOS. The mixture was poured into polystyrene Petri dishes (5 mL/60 mm Petri dish) after stirring for 90 min at atmospheric temperature, followed by evaporation under ambient conditions giving rise to free-standing NCC/silica composite films. The CNMS films were obtained by calcining the NCC/silica composite films at 540 ˚C for 6 h in muffle furnace at a heating rate of 2 ˚C·min^{-1}. The CNMS films which give a strong red color are designated as CNMS-1 with the ratio of 1.65 ml TMOS / 20 ml to 3.5% NCC (7g TMOS / 3g NCC). CNMS-2 and CNMS-3 were prepared using the same procedures under from mixtures containing 4g TMOS / 3g NCC and 3g TMOS / 3g NCC, respectively.[2]

Supporting Characterization

The emission spectra of CNMY-n and REF-n were obtained under the excitation of 395 nm that is the intrinic excitation of Eu^{3+}. The excitation at 260 nm was selected for monitoring the transition of $^5D_0 \rightarrow {}^7F_2$ of CNMY-n and REF-n at the room

temperature, luminescent decay dynamics as 260 nm can ensure all the Eu^{3+} ions be excited. The polarized emission spectra of CNMY-n were recorded under the excitation of 464 nm as it is in the range of polarization beam splitter (450-750 nm).

Supporting Figures and Tables.

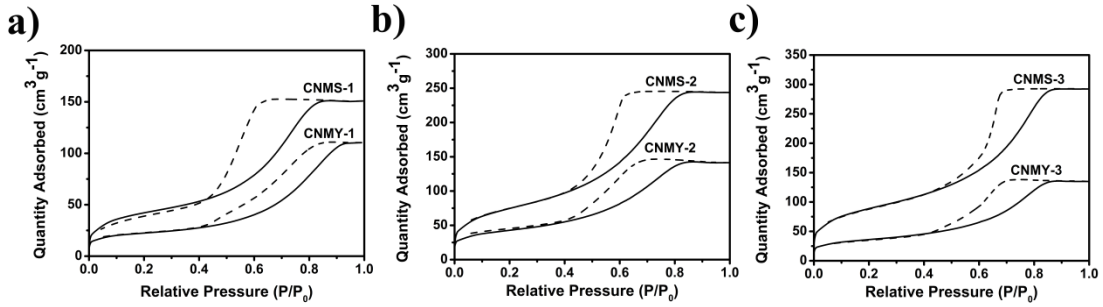

Figure S1. Nitrogen adsorption-desorption isotherms of CNMS-n and CNMY-n (n=1-3), respectively.

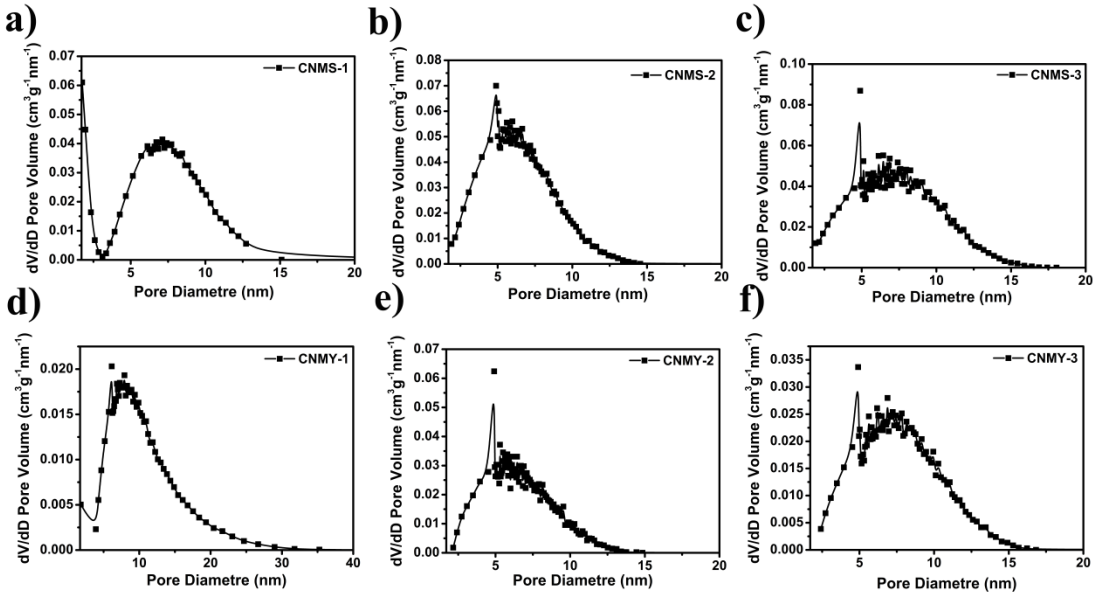

Figure S2. BJH pore size distributions based on the adsorption branch of N_2 isotherms for (**a**) CNMS-1, (**b**) CNMS-2, (**c**) CNMS-3, (**d**) CNMY-1, (**e**) CNMY-2 and (**f**) CNMY-3.

Table S1. BET surface areas, pore diameter and pore volume of CNMS-n and CNMY-n (n=1-3).

Sample	BET surface area (m^2g^{-1})	BJH pore diameter (nm)	Pore volume (cm^3g^{-1})
CNMS-1	146.5	7.4	0.27
CNMY-1	74.3	9.3	0.24
CNMS-2	263.7	6.6	0.43
CNMY-2	146.3	8.3	0.30
CNMS-3	310.2	6.9	0.54
CNMY-3	122.5	9.2	0.28

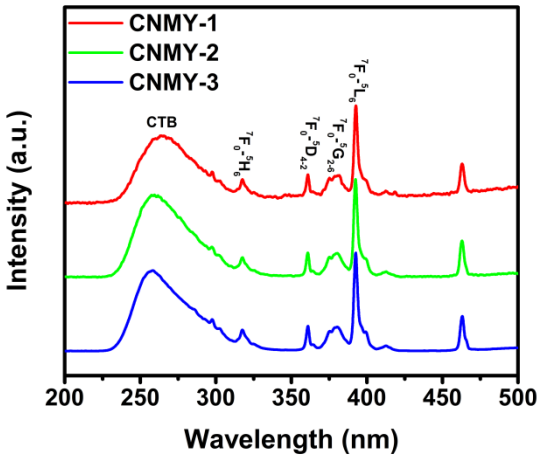

Figure S3. Normalized excitation spectra of CNMY-n (n=1-3) monitored at 612 nm.

Table S2. The fluorescence lifetime for CNMY-n and corresponding REF-n (n=1-3) at λ_{ex}= 260 nm.

Sample	CNMY-1	REF-1	CNMY-2	REF-2	CNMY-3	REF-3
Decay Time, τ/ms λ_{em}= 612 nm	1.863	1.745	1.934	1.766	2.035	1.791

Table S3. The fluorescence lifetime for CNMY-n (n=1-3) recorded at 464 nm excited with common light and linear polarized light, respectively.

Sample	Decay time, τ/ms λ_{em}= 612 nm	
	Common Light	Linear Polarized Light
CNMY-1	1.625	1.614
CNMY-2	1.568	1.572
CNMY-3	1.789	1.763

Reference:

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.