Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

Photonic structuring improves colour purity of rare-earth nanophosphors

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Materials and methods

Chemicals: Gadolinium(III) nitrate hexahydrate ($Gd(NO_3)_3\cdot 6H_2O$, Aldrich, 99.9%), europium(III) nitrate pentahydrate ($Eu(NO_3)_3\cdot 5H_2O$, Aldrich, 99.9%), sodium orthovanadate (Na_3VO_4, Aldrich, 99.9%), polyacrylic acid (PAA, Aldrich, average $M_w \approx 1800$), ethylene glycol (EG), zirconium (IV) *n*-propoxide 70% in 1-propanol (Aldrich), tetraethyl orthosilicate (TEOS, Aldrich), triblock copolymers Pluronic® F127 ($M_w \approx 12600$), 2,4-Pentanedione (acetylacetonate, acac, AlfaAesar), SiO_2 (LUDOX TMA, Aldrich), absolute ethanol, methanol, HCl (3.571mol/l, Panreac) and MilliQ water.

Nanophosphor Synthesis: In the present work, the solvothermal method was used to synthesize the $GdVO_4$: Eu^{3+} nanophosphors.[1] Suitable amounts of RE nitrates were dissolved in ethylene glycol (2.5 ml). The doping concentration of Eu^{3+} in the $GdVO_4$ host was fixed at 10% in molar ratio. To facilitate the dissolution of reagents in ethylene glycol (EG) the solutions were mildly heated (~ 80 °C) under magnetic stirring. In a separate vial, a weighted amount of Na_3VO_4 and 2 $mg\cdot ml^{-1}$ of PAA were dissolved in an EG–H_2O mixture (1 ml EG + 1.5 ml H_2O). After cooling down to room temperature, both solutions were then admixed while keeping the magnetic stirring. In the final solutions, the total RE and the Na_3VO_4 concentrations were kept constant at 0.02 $mol\cdot L^{-1}$ and 0.1 $mol\cdot L^{-1}$, respectively whereas the final EG–H_2O volumetric ratio was 3.5:1.5. The as-prepared solutions were then aged for 3 h in tightly closed test tubes using an oven preheated at 120 °C. Then, the resulting dispersions were cooled down to room temperature, centrifuged to remove the supernatants and washed twice with ethanol and once with distilled water. Finally, the precipitates were re-dispersed in methanol with a concentration of 1% wt.

ZrO_2 Precursor Sol Synthesis: Briefly, a mix of ethanol, acac, zirconium *n*-propoxide, HCl, water and F127 in a molar ratio of 40:1:1:1:20:0.005 is prepared. Zirconium propoxide, acac and F127 were dissolved in 80% of the total ethanol and the mixture was stirred for one minute. HCl and water dissolved in the remaining ethanol were added dropwise while stirring to the first solution. The final sol was then stirred during one hour.

SiO_2 Precursor Sol Synthesis: For the synthesis of the SiO_2 sol, we used 9 ml of tetraethyl orthosilicate and 68 ml of absolute ethanol. After some minutes under vigorous stirring, 3.44 ml of H_2O and 0.16 ml of HCl (0.05 $mol\cdot L^{-1}$) were added. The resultant solution was stirred overnight before use.

Deposition of Optical Multilayers: Optical multilayers were fabricated by the alternated deposition of layers prepared with ZrO_2 precursor sol and SiO_2 nanoparticle suspension (1% wt in methanol) using a dip-coater. The SiO_2 dense layer was employed to prevent the infiltration of the ZrO_2 precursor sol into SiO_2 and $GdVO_4$: Eu^{3+} nanoparticle layers, which are inherently porous. To guarantee the same optical property of both sides of photonic crystal, the first and the last layers were ZrO_2 ocatings. The withdrawal speeds of the substrate in ZrO_2 sol, SiO_2 nanoparticle suspension, SiO_2 sol and nanophosphor suspension were 120, 120, 50 and 120 $mm\cdot min^{-1}$, respectively. The multilayer starts with the deposition of the ZrO_2 sol on top of a clean zero-fluorescence microscope glass slide. This first layer was treated at 500 ^{o}C for 30 minutes. Next, a layer of SiO_2 nanoparticles is deposited on top of the ZrO_2 layer in several steps of the same suspension to increase its thickness with a waiting time of 60s between dips to ensure solvent evaporation. After that, a dense SiO_2 layer was coated with a soaking time of 30s in the corresponding precursor sol, then a 10 min of heat treatment at 500 ^{o}C was followed to stabilize the layer. This process is repeated until five unit cells were deposited. Then, a nanophosphor layer sandwiched between two ZrO_2 layers was coated in several steps with a 5 min of heat treatment at 400^{o}C between dips to build an optical cavity. Another five unit cells were deposited after the sample cooled down to room temperature. For the sake of comparison, a $GdVO_4$: Eu^{3+} nanophosphor layer sandwiched between two ZrO_2 was also prepared for referencing purpose.

Structural characterization: The crystalline structure of as-prepared nanophosphors was investigated by X-ray diffraction using a Panalytical, X' Pert Pro diffractometer. The shape of the nanoparticles was examined by transmission electron microscopy (TEM, Philips 200CM).

FESEM images of the multilayer films deposited onto glass were taken by using a microscope Hitachi S4800.

Calculations: The spectral dependence of the spatial distribution of the electric field intensity was calculated using an in-house code based on the transfer matrix approach. A genetic algorithm was employed to find the structural parameters that yield a targeted optical response.

Optical characterization: The excitation and emission spectra as well as the lifetime of these samples were measured with a Horiba JobinYvon spectrofluorometer (Fluorolog FL3-11). Reflectance spectra were measured using a Cary 7000 series UV-Vis-NIR spectrophotometer.

Figures

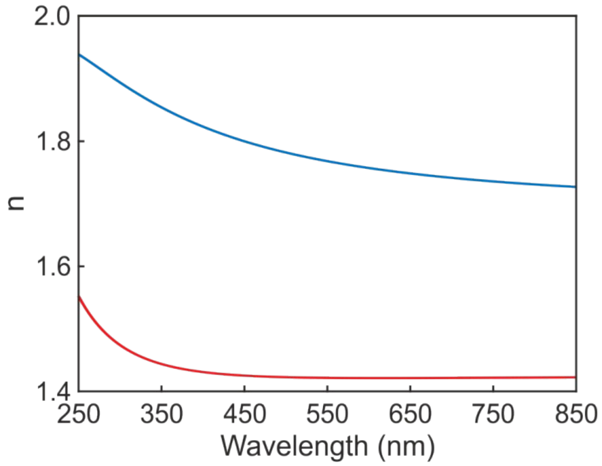

Figure S1 Estimated spectral dependent refractive index of ZrO_2 (blue) and SiO_2 (red).

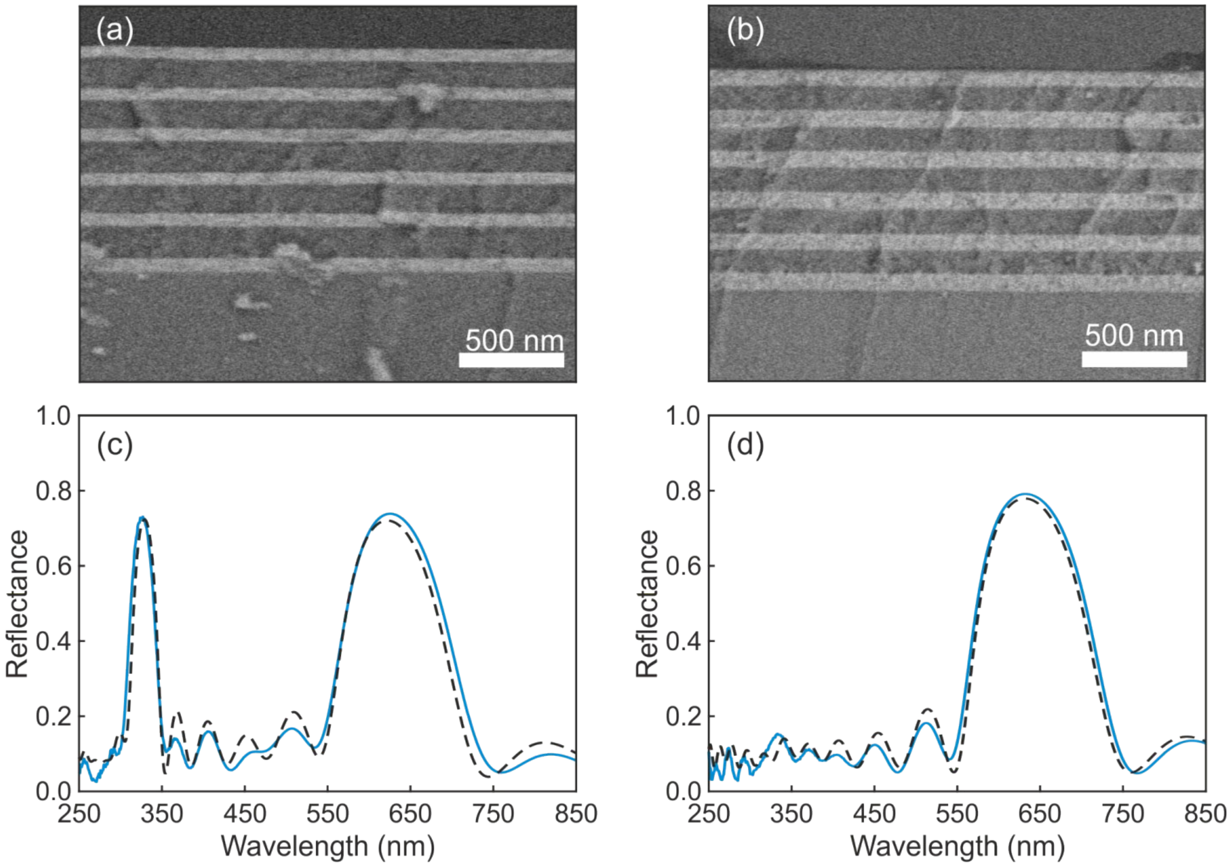

Figure S2 FESEM images of the cross section (a and b) and the corresponding reflectance spectra (c and d) of two different Bragg stacks. Spectrum displayed in (c) shows both first and second diffraction order whereas the second order has been suppressed in (d) Dash lines correspond to the optimized fitting for each spectrum. The thicknesses of ZrO_2 and SiO_2 layers were calculated to be 66 nm and 140 nm, respectively in (c), and 87 nm 116 nm, respectively, in (d).

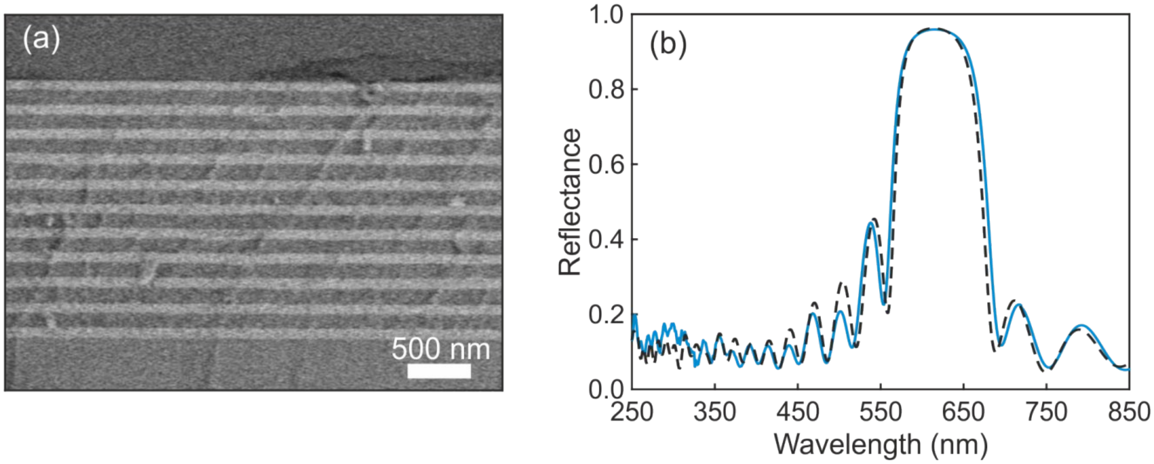

Figure S3 FESEM images of the cross section (a) and the corresponding reflectance spectrum (b) of the photonic multilayer employed to build the optical resonator displayed in Figure 3 of the main manuscript. Dash line in corresponds to the optimized fitting for the spectrum. The thicknesses of ZrO_2 and SiO_2 layers were calculated to be 85 nm and 110 nm, respectively.

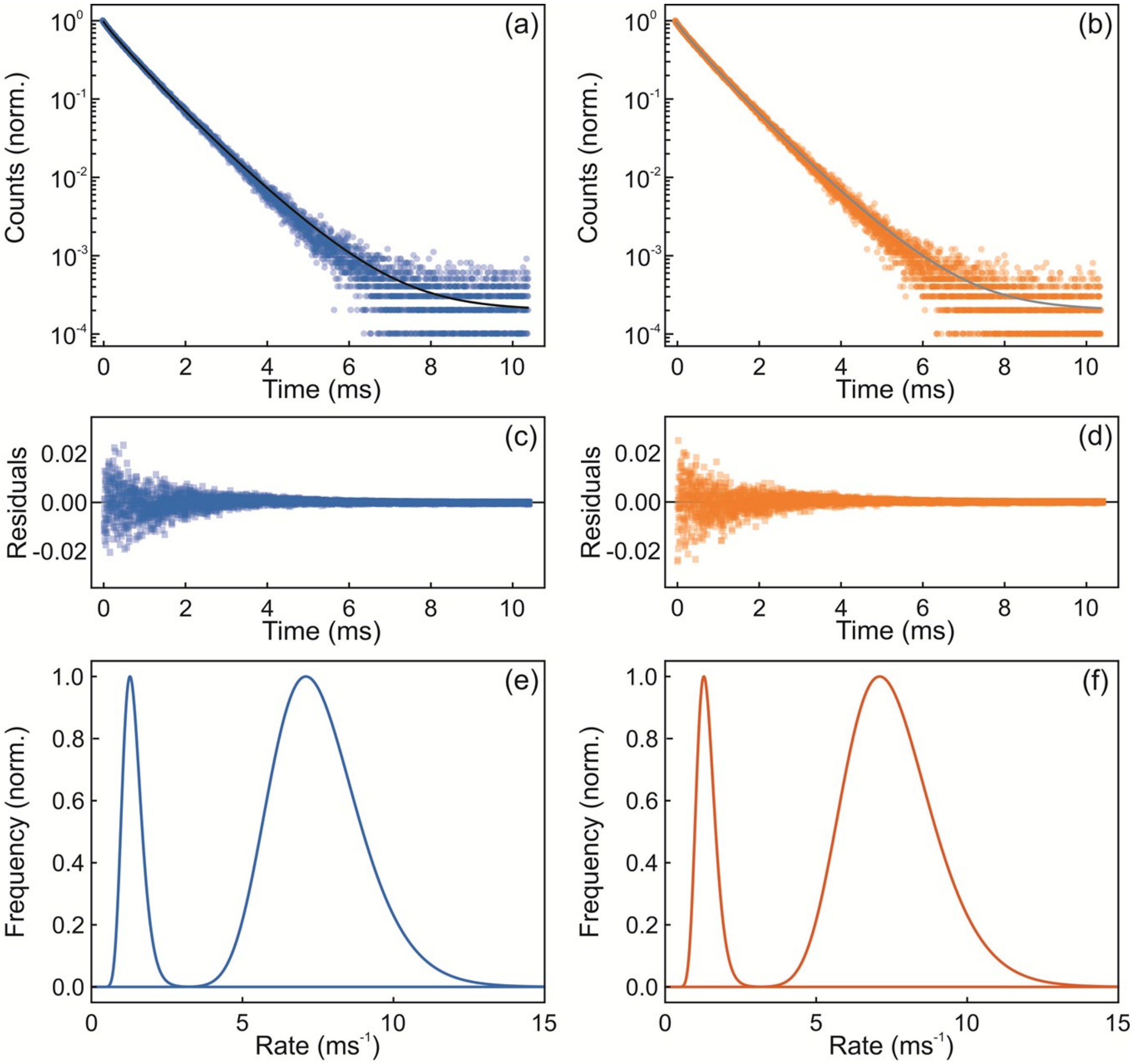

Figure S4. (a-b) Time dependence photoluminescence of Eu^{3+} cations in a reference layer (orange, b) and integrated in the resonator (blue symbols, a) together with their corresponding fits to a sum of two log-normal distributions of decay rates (grey and black solid lines, respectively). (c-d) Residuals of the fits shown in (a) and (b), respectively. (e-f) Log-normal distributions of decay rates corresponding to the fits shown in (a) and (b), respectively.

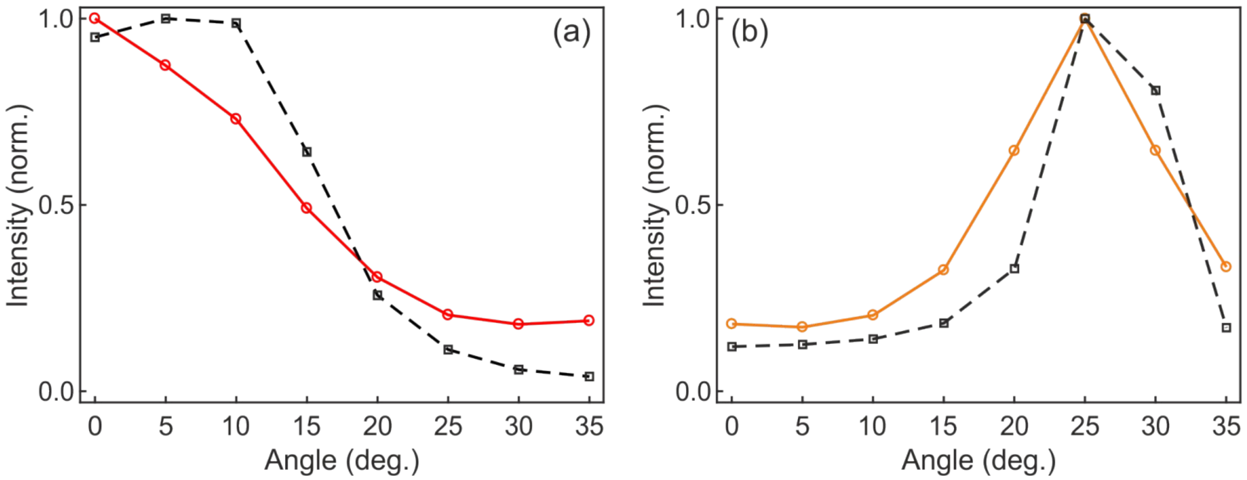

Figure S5 Experimental (color dots) and calculated (black dots) angular dependence of the red (a) and orange peaks (b) of the resonator whose angular reflectance is shown in Figure 4 (a). Lines are only guides to the eye.

References

1. N. O. Nuñez,, S. Rivera, D. Alcantara, J. M. de la Fuente, J. García-Sevillanoc and M. Ocaña, *Dalton Trans.*, 2013, **42**, 10725-10734.