Electronic Supplementary Information

Collective plasmonic resonances enhance the photoluminescence of rare-earth nanocrystal films processed by ultrafast annealing

Elena Cabello-Olmo,[a] Makoto Higashino, [b] Shunsuke Murai,*[b] Katsuhisa Tanaka,[b] Gabriel Lozano*[a] and Hernán Míguez[a]

** Corresponding authors.*

[a] *Instituto de Ciencia de Materiales Sevilla, Consejo Superior de Investigaciones Científicas-Universidad de Sevilla, Americo Vespucio 49, 41092, Spain.*
Email: *g.lozano@csic.es*

[b] *Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.*
Email: *murai@dipole7.kuic.kyoto-u.ac.jp*

Materials and Methods

Fabrication

Materials. Chemicals used for the synthesis of nanophosphors were 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%), poly(acrylic acid) (PAA, Aldrich, average Mw ≈ 1800), ethylene glycol (EG). The materials used for the fabrication of the sticker were Polyvinylpyrrolidone (PVP, Aldrich, average Mw ≈ 40,000), resist (TU7-170) and the polydimethylsiloxane (PDMS) was prepared with DOWSILTM SILPOT 184 Dow.

Nanophosphor synthesis. $GdVO_4:Eu^{3+}$ nanoparticles were synthesized following a solvothermal method reported somewhereelse.[1] Concretely, Eu^{3+} cations are introduced as substituents of Gd^{3+} with a concentration of 10% ($Gd_{0.9}VO_4Eu_{0.1}$). In short, NPs are obtained through homogeneous precipitation reaction of the RE precursors and sodium orthovanadate in EG/water mixture at 120°C. PAA was added during the synthesis as functionalization agent. Finally, NPs are dispersed in methanol.

Film preparation. Nanophosphor thin films were prepared via spin-coating using the following deposition parameters: final speed 3000 rpm, acceleration 11340 rpm s^{-1}, time 1 minute. The deposition was repeated three times to achieve 250 nm-thick films.

RTA processing. RTA was done in O_2 flow using a gold image furnace (MILA-5050, ADVANCE RIKO). Notice that it takes 16 hours for a film to go from room temperature to 1000 °C with a heating rate of 1 °C per minute in a conventional oven. RTA in turn provides ultrafast thermal processing. In this case, we heat nanophosphor films using a rate of 10°C per second until they reach 1000°C (and kept for 5 min).

Plasmonic sticker preparation. Al nanoparticle arrays were fabricated using nanoimprint lithography (EntreTM3, Obducat) and reactive ion etching (RIE) (RIE-101iPH, Samco). First, an EtOH solution of PVP(7 wt%) was coated onto an SiO_2 glass substrate and prebaked for 10 min at 80°C. Al thin film (thickness = 50 nm) was grown on the PVP layer (∼ 500 nm) using electron beam deposition. The resist (TU7-170) was then coated onto the Al thin film and prebaked for 5 min at 95°C. Separately, using electron-beam lithography (F7000s-KYT01, Advantest) and Si deep etching (RIE-800iPB-KU, Samco), the Si master mold which consisted of square pillar array was fabricated over 6 mm × 6 mm area. This nanopattern was transcribed to the resist on the Al thin film. Subsequently, excess photoresist was removed by O_2 plasma ashing (RIE-10NR-KF, Samco). Finally, the Al nanoparticle array whose geometry was similar to the pattern of the Si master mold was obtained using RIE under a chamber pressure of 0.1 Pa, a radio frequency power of 150 W and both N_2 and Cl_2 gas flow rates of 5 cm^3/min. Transfer of Al nanoparticle arrays from glass substrate to polydimethylsiloxane film was performed by wet etching using water. PDMS film (DOWSILTM SILPOT 184 Dow) was prepared by mixing weighing base and curing agent with a ratio of 10:1 using a rotation revolution mixer (ARE-310 THINKY). The mixture was cast onto the Al nanoparticle array on the glass (thickness ∼ 2 mm), degassed under vacuum for 40 min at 35 °C and then cured for 2 h at 80 °C. The array with a PDMS film on the top was soaked in distilled water for one day to dissolve the PVP layer. Finally, the PDMS film embedded with the Al nanoparticle array was peeled off from the glass substrate.

Characterization

Structural characterization. SEM images were taken using microscopes Hitachi S4800 and Hitachi SU8000. A Pt layer was deposited as a conducting layer before the measurement of the plasmonic stickers. AFM images were taken by using AFM PicoPlus 2500. X-ray diffractions were measured with a diffractometer (SmartLab, Rigaku) with Cu Kα line as the source. Crystallite sizes were calculated from the most intense reflection peak (200) by using the Scherrer equation.

Optical characterization. Absolute PLQY and time-dependent PL were measured with Edinburgh FLS1000 spectrofluorometer. PLQY values were measured using an integrating sphere and a xenon lamp by calculating and ratio between emitted photon counts and the absorbed photons counts. The absorbed photons were extracted from the comparison of the scattering of the excitation (285nm, bandwidth=10nm) for both the samples and an uncoated quartz substrate. The time-dependent measurements were performed with a pulsed xenon flashlamp at repetition rate of 50 Hz using MCS method.

Transmittance and angular Extinction. The ballistic optical transmission close to the normal incidence (θ_{in} = 6°) was measured using an UV-vis-IR spectrophotometer Cary 7000. Angular-varied extinction spectra were measured as a function of angle of incidence θ_{in} with a spectrometer (Flame, Ocean Optics). The sample was set on a rotation stage to vary θ_{in} on the sample surface. Extinction was defined as 1- T/T_0, with T and T_0 being the measured zeroth-order transmission of the sample and the reference, respectively.

Angular photoluminescence angular spectra were taken in a double goniometer mounted in an optical table. The samples were excited with a 285 nm LED (FWHM = 13 nm, power = 50 mW) and the emitted light was recollected with a fiber-coupled spectrophotometer (Ocean Optics USB2000+VIS-NIR-ES).

Fourier microscopy was performed by back focal plane imaging. The microscope setup has a halogen lamp used to focus and illuminate the samples in the reflectance configuration. An objective with 0.75 numerical aperture was used. At the entrance of the CCD, an optical filter centred at 620 nm (FWHM=19 nm) was placed to discriminate the emission from the less intense emission peaks and to resolve spectrally the reflectance images. For the PL configuration, the samples were excited with a UV lamp from the substrate.

Calculations

FDTD calculations were performed using the commercial software Ansys Lumerical FDTD. The calculations were done considering a unit cell and periodic boundary conditions, and using nominal values for the geometrical parameters of the nanophosphors films and nanodisks. Both substrate and the PDMS are simulated as infinite media with Perfectly Matched Layer conditions. The effective refractive index of the phosphors films was estimated by using Abeles Transfer Matrix Method using experimental data of the reflectance and transmittance at different angles of incidence together with the measurement of the diffuse reflectance and transmittance. The code for estimating the optical constants of an arbitrary layered optical material can be found in the Data Availability section of the Communication.

AFM images

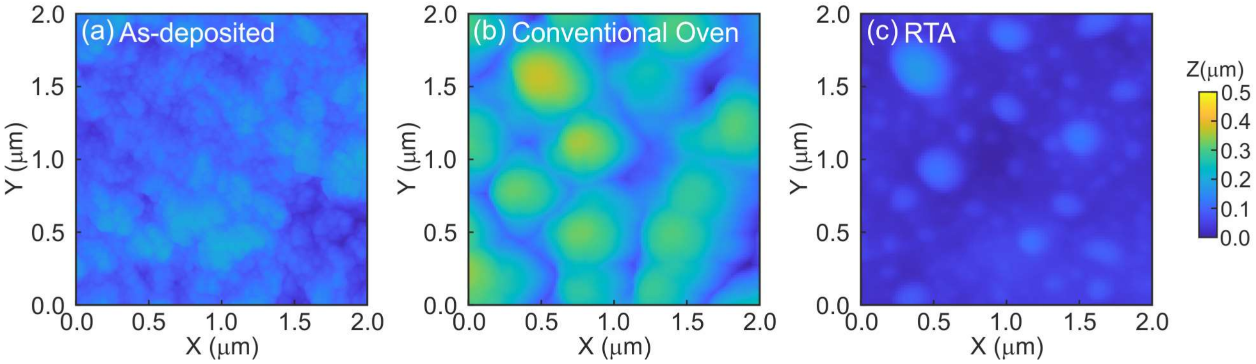

Figure SI 1: Atomic force microscope (AFM) topography of the surface of the nanophosphor film as-deposited (a), and annealed at 1000 °C in a conventional oven (b) or using RTA (c).

XRD analysis

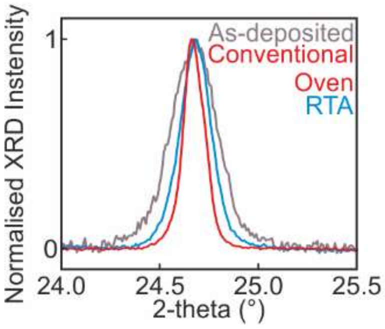

Figure SI 2.: Normalised XRD Intensity in a small angular range for a film as-deposited (grey) and the same films after processing at 1000 °C in a conventional oven (red) and using rapid thermal annealing (blue).

Time-dependent Photoluminescence Analysis

	τ_1 (ms)	w_1	τ_2 (ms)	w_2	τ_{aver} (ms)
As-deposited	0.31	22.5 %	0.92	77.5 %	0.782
1000 RTA	0.37	9.4 %	0.82	90.6 %	0.778
1000 conv	0.38	19.0 %	0.73	81.0 %	0.662

Table SI 1: Two-exponential model fitting parameters of the Time-Dependent Photoluminescence measured from nanophosphor Films.

SEM images of the plasmonic stickers

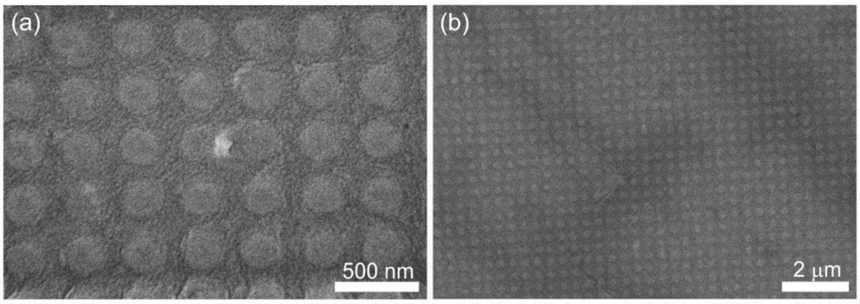

Figure SI 3: Scanning electron micrographs of the top view of the array of metallic NPs embedded in a PDMS film.

Comparison of the extinction of plasmonic arrays deposited atop nanophosphor films processed by conventional and rapid thermal annealing

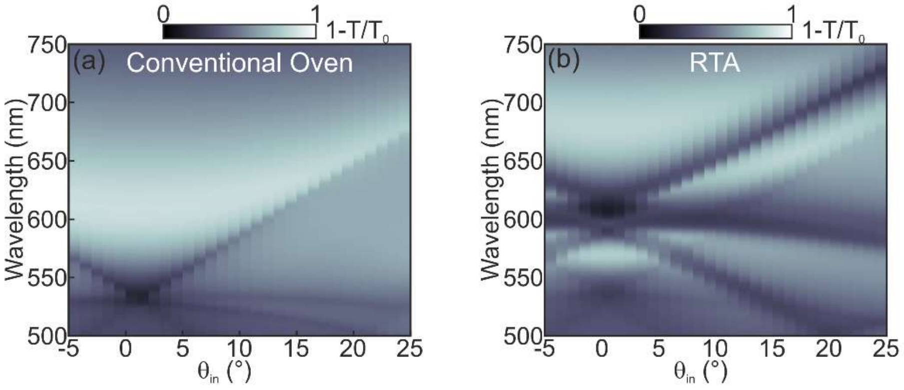

Figure SI 4: Comparison of the angular dependence of the extinction spectra measured from two emitting films annealed at 1000 °C by conventional (a) and rapid thermal annealing (RTA) coated with the same plasmonic sticker (b). Notice that only RTA leads to the excitation of plasmon modes.

Angular dependent emission profile for the main transitions of Eu^{3+}

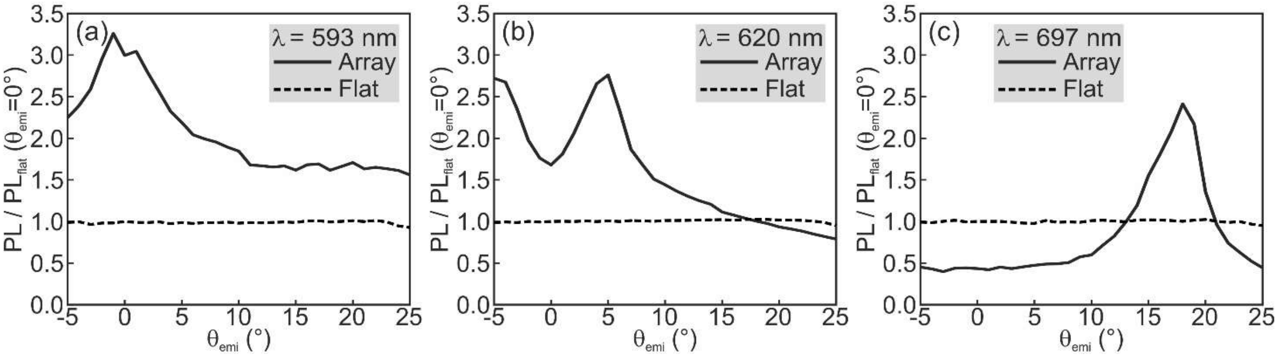

Figure SI 5: Angular-dependent photoluminescence of a plasmonic-based nanophosphor film at the spectral position of main Eu^{3+} transitions, i.e. λ = 593 nm (a), λ = 620 nm (b), and λ = 697 nm (c). Angular profile measured from a reference film devoid any plasmonic array (dashed line) is also shown for comparison. Photoluminescence intensity is normalized to that of the reference film at θ_{emi} = 0°.

FDTD calculations

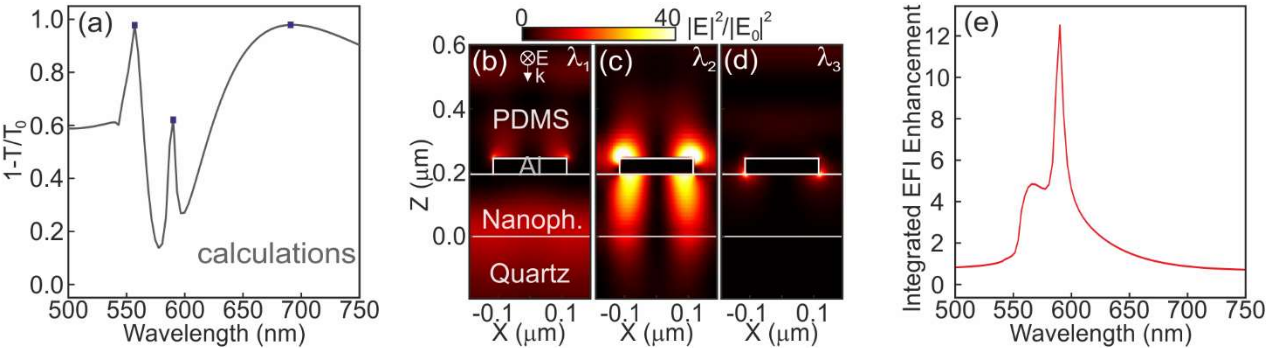

Figure SI 6. (a) Finite Difference Time Domain (FDTD) simulations of the extinction spectrum at 0°. Calculations consider a plane wave as excitation source. (b-d) FDTD calculated spatial distribution of the Electric Field Intensity at 557 nm (f), 590 nm (g) and 691 nm (h). The aluminium nanoparticle and the different interfaces are highlighted with white lines. (e) Integrated enhancement of the electric field intensity over the volume where nanophosphors are distributed divided by that of the reference.

References

1 NO Núñez *et al.*, *Dalton Trans.*, 2013, **42**, 10725.