ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Enhancement of upconversion photoluminescence in phosphor nanoparticle thin films using metallic nanoantennas fabricated by colloidal lithography

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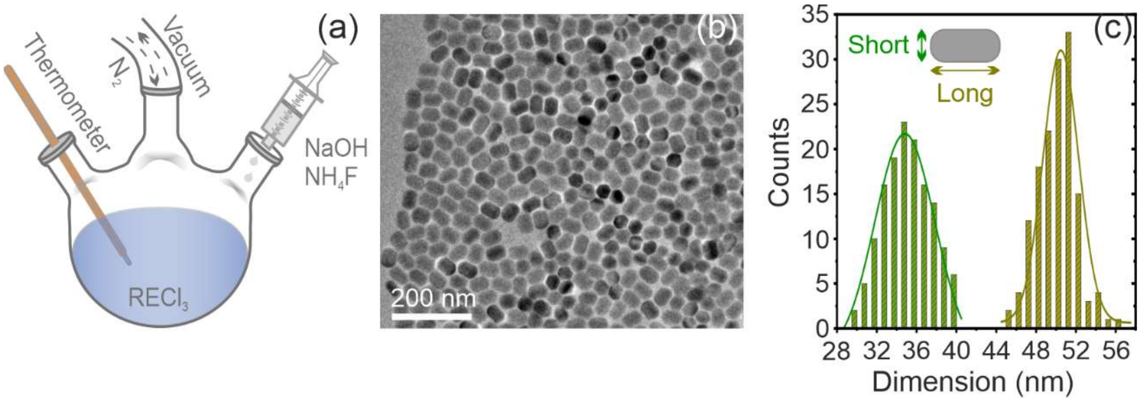

Figure S1. *(a) Schematic of the synthesis of $NaYF_4$:Yb^{3+},Er^{+3} nanoparticles (hereafter referred to as NaYF NPs). (b) TEM image, and (c) their size distribution.*

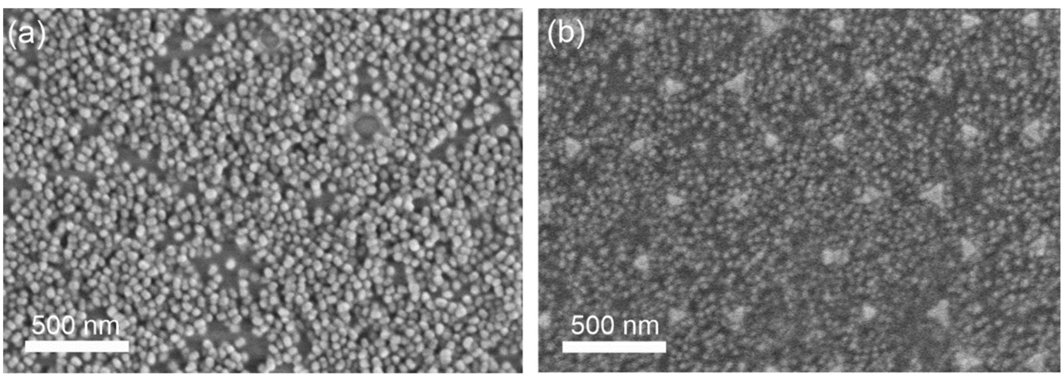

Figure S2. *(a) Scanning electron microscope (SEM) image in the secondary electron mode of a top view of a NaYF/PAA UC film deposited on glass. (b) SEM image of the same film on a gold nanoantenna array.*

Figure S3 shows the experimental specular reflectance of the Au/UC sample (black solid line) measured at normal incidence with a VIS-NIR spectrophotometer (IFS 66/S, Bruker). The LSPR appears at ~1000 nm. The calculated reflectance (gray dashed line) shows good agreement with the experiment. The difference between the measured and calculated reflectance is due to the fact that the calculations do not take scattering into account.

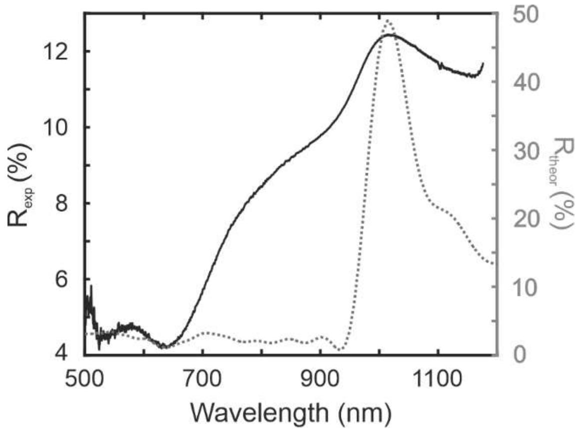

Figure S3. *Experimental (black solid line) and theoretical (grey dashed line) reflectance of a UC film on a gold nanoantenna array.*

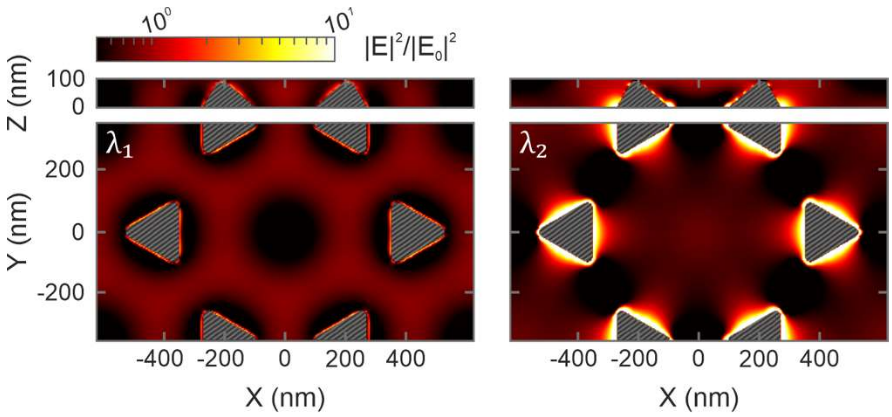

Figure S4. *Finite difference time domain (FDTD) simulated electric field intensity for the Au/UC sample at λ_1=540 nm and λ_2=665 nm. Two sections are shown: XY plane (z=0 nm) and YZ plane (intersecting two of the nanoantennas).*

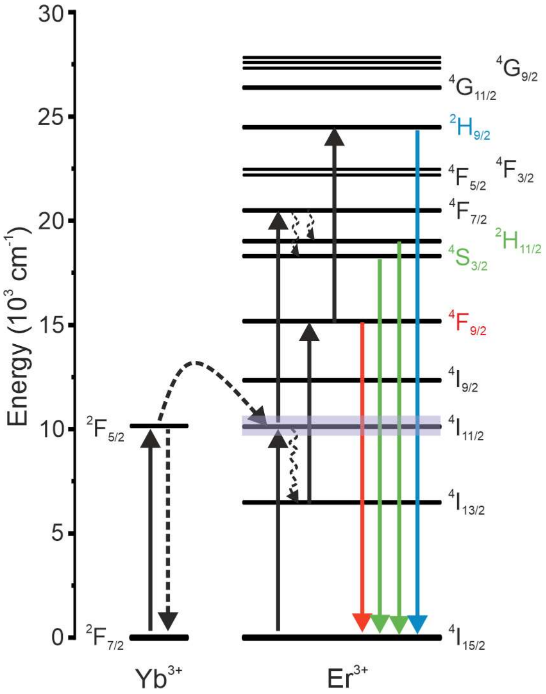

Figure S5*. Energy level diagram of Yb^{3+} and Er^{3+} ions. Data are taken from Ref.[1].*

Figure S6 shows the integrated UCPL intensity as a function of the pump power density. The UCPL intensity shows a quadratic power dependence. However, a reduction in the slope is observed in the presence of the nanoantennas. Specifically, it decreases from 2.0 to 1.7 and from 2.3 to 2.0 for the green and red emission bands, respectively. LSPRs can accelerate the energy transfer from the $^2F_{5/2}$ energy level of Yb^{3+} to the $^4I_{11/2}$ of Er^{3+} emitters.[2]

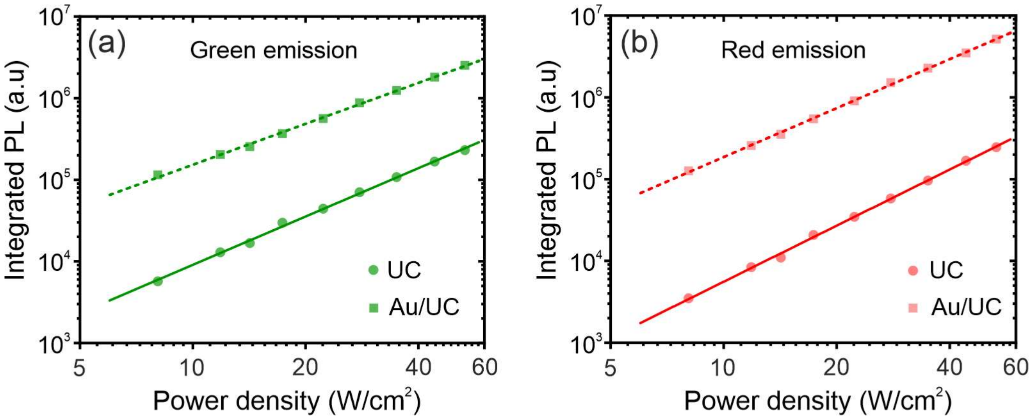

Figure S6. *Power dependence of UCPL intensity for (a) the green (integrated between 510-575 nm) and (b) the red (integrated between 630-695 nm) emission bands of a UC reference film (round symbols) and that of the same film deposited over a nanoantenna array (square symbols). A continuous 980-nm laser is used as the excitation source, and neutral filters are used to adjust the power density.*

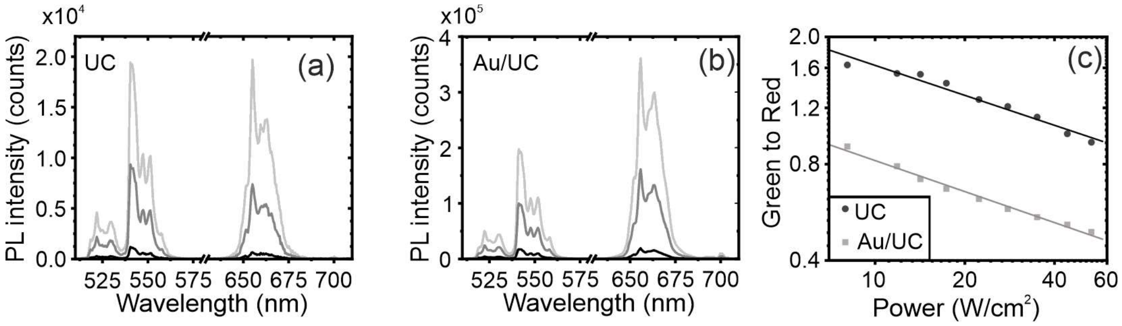

Figure S7. *(a-b) UCPL intensity spectra of UCNP thin films deposited on a glass substrate (a) and that of the same film deposited on a nanoantenna array (b) measured at different excitation power densities: 11.8 (black), 35 (dark grey) and 53.2 W/cm^2 (grey). (c) Green (integrated between 510-575 nm) to red (integrated between 630-695 nm) emission intensity ratio as a function of the excitation power density. A continuous 980 nm laser is used as the excitation source, and neutral filters are used to adjust the power density.*

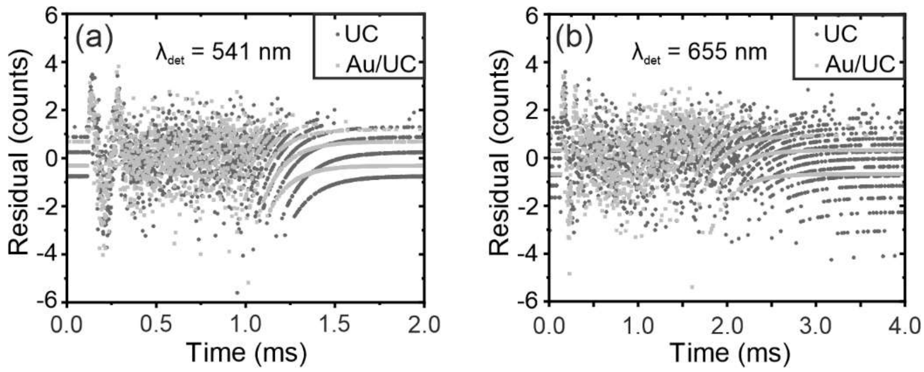

Fig S8*. (a-b) Residuals of the fits presented in Fig. 3c and Fig 3d, respectively.*

Figure S9 summarizes the results we have obtained on UCNP thin films deposited on silver nanoantennas. Silver nanostructures support LSPRs, as confirmed by numerical simulations, which overlap with the emission bands of NaYF. The IIE calculation shows a value of ~9 at ~980 nm, higher than that of gold nanostructures of similar dimensions. Thus, the UCPL enhancement is expected to be higher. Specifically, silver nanoantennas induce a UCPL intensity enhancement values up to ~30 and ~50 times for high power densities for green and red emission bands, respectively.

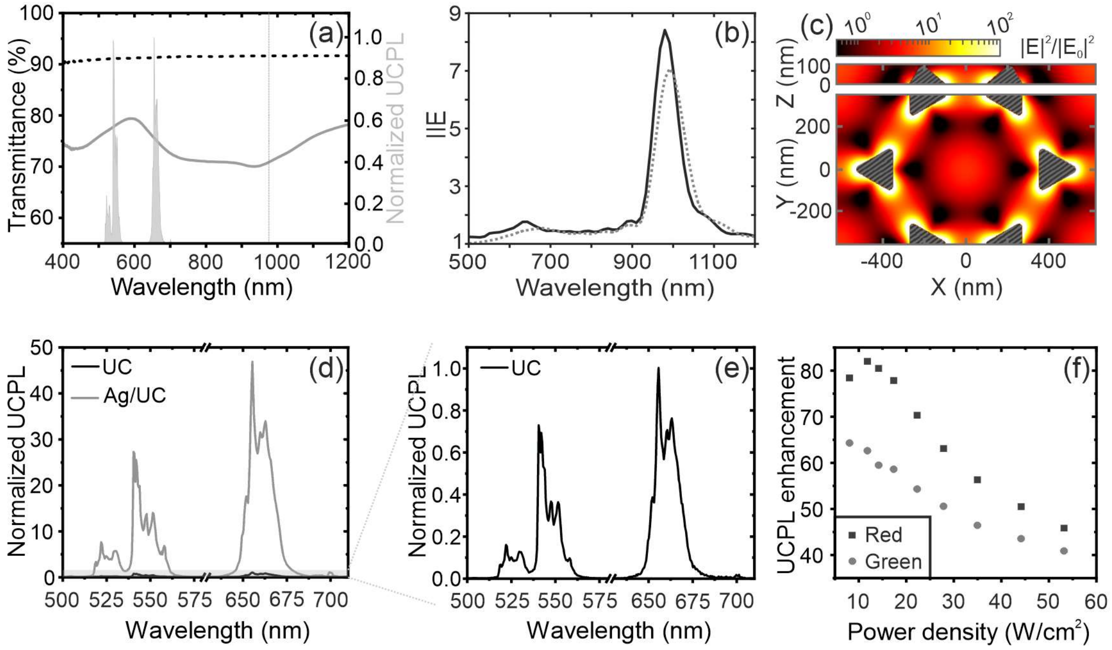

Figure S9. *(a) Transmittance of a UCNP thin film deposited on glass (black dashed line, denoted as UC) and that of the same film deposited on a silver nanoantenna array (grey solid line, denoted as Ag/UC). The UCPL spectrum of NaYF NPs is shown as grey bands. The excitation wavelength (980 nm) is also shown as grey dashed line. (b) Integrated intensity enhancement (IIE) for a UC film on a gold (dotted line) or a silver (solid line) nanoantenna array. (c) Simulated electric field intensity for the Ag/UC sample at the wavelength of 980 nm. Two spatial profiles are shown: XY plane (z=0 nm) and YZ plane (intersection of two of the nanoantennas). (d) UCPL intensity spectra of the UCNP thin film deposited on glass (black line) and that of the same film deposited on the silver nanoantenna array (grey line) at an excitation of 53 W/cm^2. The UCPL intensity is normalized to that of the reference UCNP film at 655 nm. (e) Zoom of (d) to show the emission of the reference UCNP film. (f) UCPL enhancement of the green (510-575 nm) and red (630-695 nm) bands at different excitation power densities. A continuous 980nm laser is used as the excitation source.*

References

1 V.S. Sastri, Jean-Claude Buzli, V. Ramachandra Rao, G.V.S. Rayudu and J.R. Perumareddi, *Modern Aspects of Rare Earths and Their Complexes*, Elsevier, 2003.

2 T. T. Ngo, G. Lozano and H. Míguez, *Mater. Adv.*, 2022, **3**, 4235–4242.