Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information (ESI) for PCCP

Enhancing the Upconversion Photoluminescence of Hexagonal Phase $NaYF_4:Yb^{3+}$, Er^{3+} Nanoparticles by Mesoporous Gold Films

Heng Qin[a], Ahmed E. Shamso[a], Anthony Centeno[b], Ioannis G. Theodorou[a], Andrei P. Mihai[a], Mary P. Ryan[a*], Fang Xie[a*]

Department of Materials and London Centre for Nanotechnology, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom

*To whom correspondence should be addressed.

E-mail: m.p.ryan@imperial.ac.uk or f.xie@imperial.ac.uk

Electromagnetic Study of Upconversion Photoluminescence

The mesoporous structure is fairly random in morphology making it difficult to model using computational electromagnetic techniques. Nevertheless, some insight can be gained by considering a structure with Periodic nanoholes with similar diameter to those of the average pore sizes. Here Finite Difference Time Domain (FDTD)[1] is used and the metal considered is 100% Au. A Drude-Lorentz model for Au is used[2]. The centre-to-centre spacing of the nanoholes is 140% of the hole diameter, and the thickness of the Au film 100 nm. The Au was on a glass slide with an 8 nm Silica film on top of the Au film. Figure 1 shows the optical absorption response obtained from the calculations. The results show the Localised Surface Plasmon Resonance by a transmission peak (or absorbtion minimum) which redshifts with hole diameter between 505 nm and 547 nm. These results suggest that the transmission maxima at around 550 nm in Figure 8 of the paper are the LSPR wavelength of the mesoporous Au films. To consider whether this could lead to emission enhancement small dipoles were placed 10 nm above the Silica film, to try and replicate the emission from the upconversion nanoparticles, similar to the procedure used previously when considering metal enhanced fluorescence [2]. The results are shown in Figure S2 for dipoles placed 20 nm above the centre of the 72 nm nanohole and midway between adjacent holes (*i.e.* above the Au film). From Figure S2 is can be seen that there is little enhancement or some quenching (enhancement factor <1) around at 540 nm. For 660 nm there is some enhancement in both cases (< 2 times). The results provide further evidence that there will be negligible emission enhancement at 540 nm and some at 660 nm, consistent with the lifetime measurements.

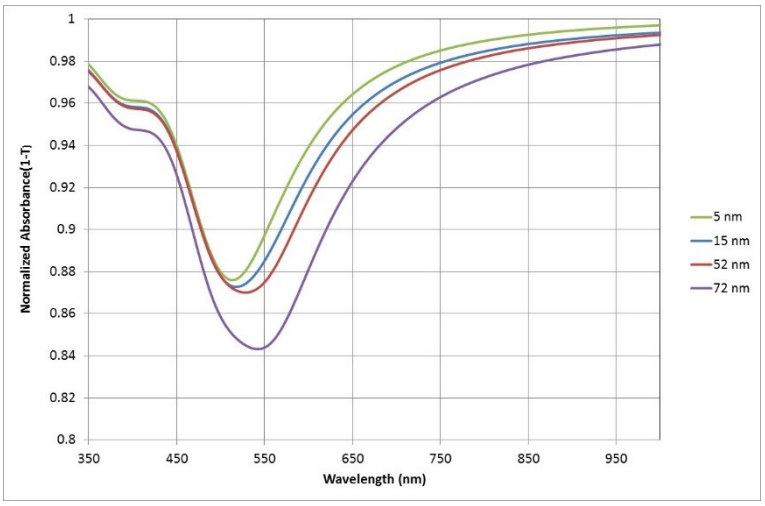

Figure S1. Absorption (1-Transmisison) for 5 nm, 15 nm, 52 nm and 72 nm nanoholes in a 100 nm Au film.

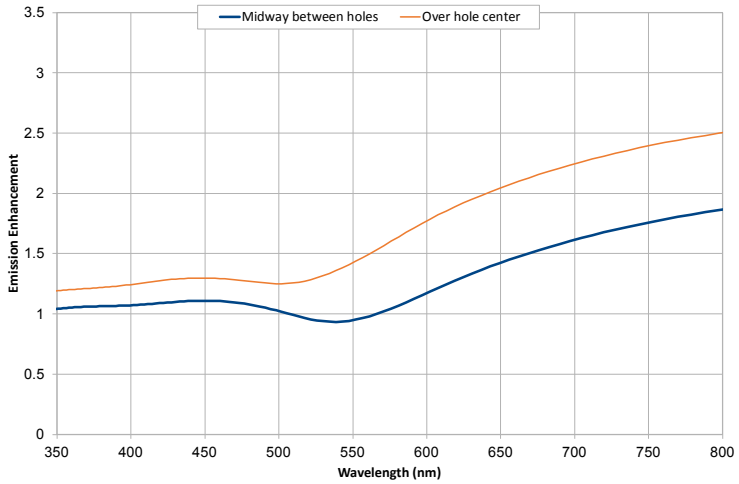

Figure S2. Enhanced emission from a small dipole placed 20 nm above the Au-Nanohole surface.

The experimental and modelling data leads us to believe that the enhancement mechanism is at the excitation wavelength. Figure S3 shows the electric field enhancement at 980 nm for the periodic nanohole array with 72 nm holes obtained from the FDTD model. It shows some e-field enhancement but not of the magnitude required to explain the experimental results. The physical mechanism of the excitation enhancement due to the mesoporous films will be investigated in future work.

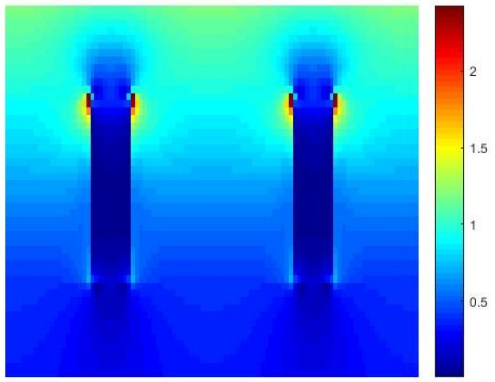

Figure S3. Electric field enhancement at 980 nm (in the cross section through the centre of the holes). The incident plane wave was polarised parallel to the Au surface.

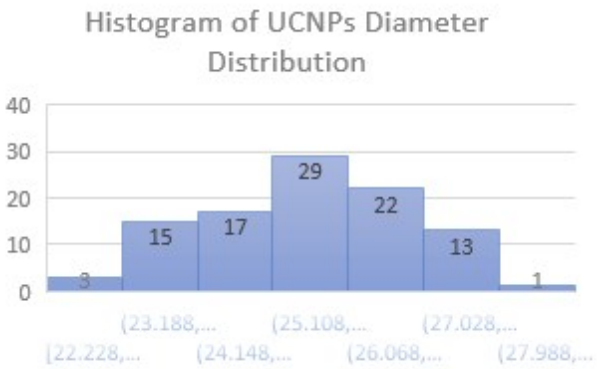

Figure S4. Histogram of UCNPs Diameter Distribution. The units of the horizontal axis are nanometers (nm).

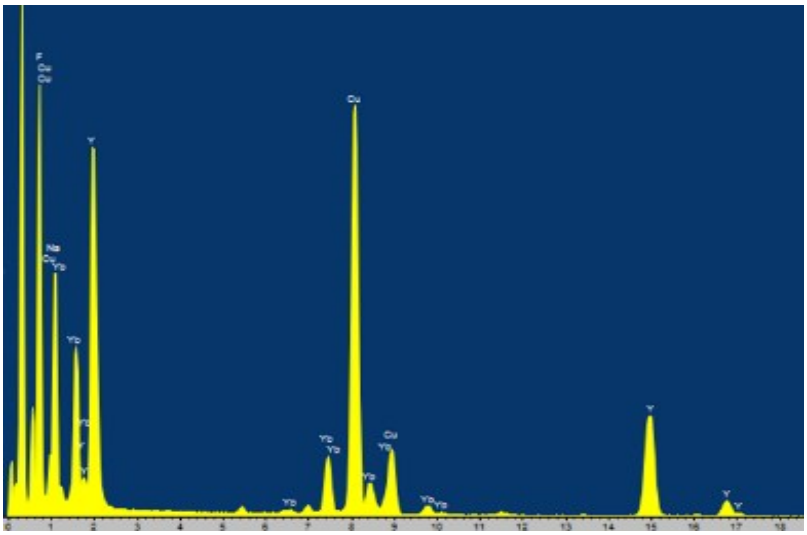

Figure S5. TEM energy dispersive X-Ray (EDX) spectrum of the UCNPs, collected from the same area as Figure 3a. The figure confirms the existence of elemental Na, Y, Yb, and F in UCNPs. The absence of Er detections was due to the very small amount of Er present in UCNPs, which was out of the limit of the instrumental sensitivity. The Cu signal element was from the copper TEM grid.

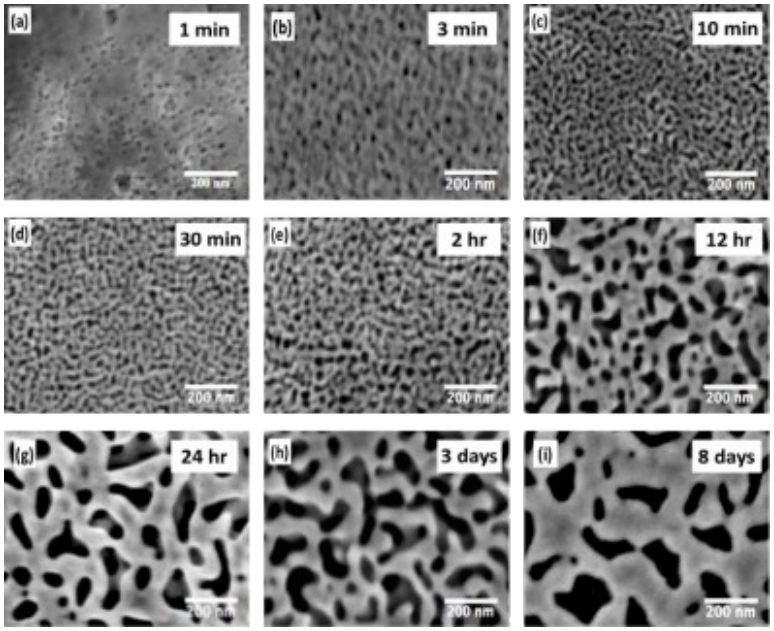

Figure S6. (a-i) Top-view SEM micrographs showing the porosity evolution of Au mesoporous films with respect to different dealloying time, ranging from 1minute to 8 days.

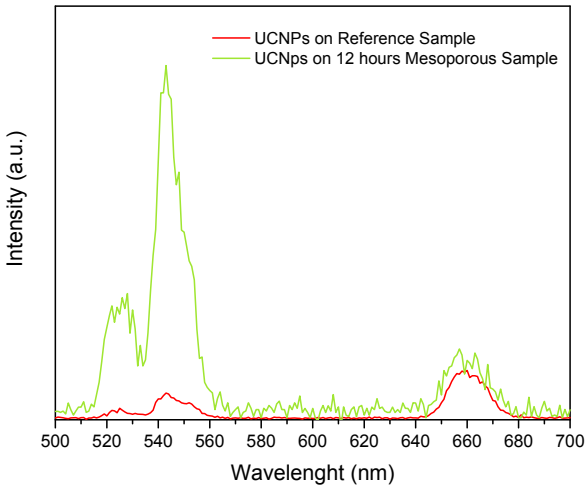

Figure S7. UCPL intensity of β-$NaYF_4$:Yb^{3+}, Er^{3+} nanoparticles on reference sample and on Au mesoporous sample with a 12-hour dealloying time, directly without any SiO_2 spacer layer. This measurement shows about 15 times quenching effect at 541 nm emission and about 1.5 times quenching effect at 656 nm emission.

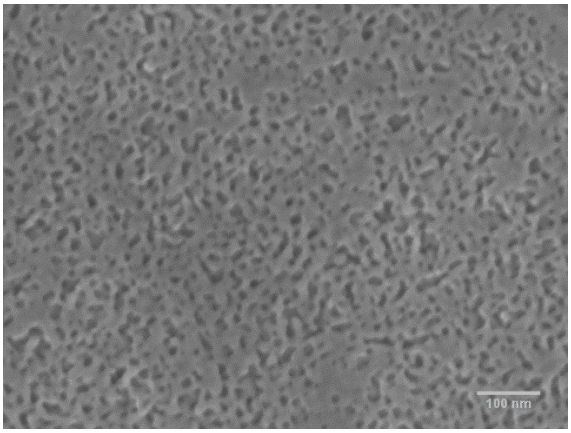

Figure S8. Top-view SEM micrographs showing the Au mesoporous film with 3 minutes dealloying time. (With 100K magnification).

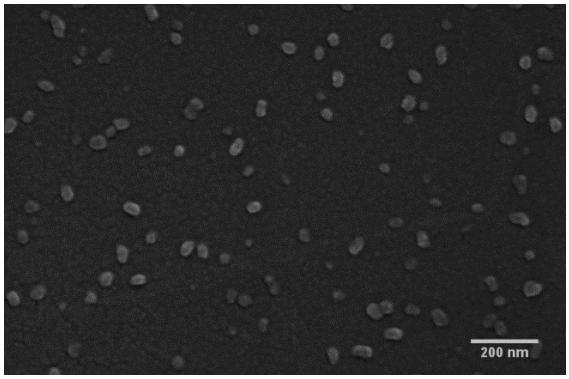

Figure S9. Top-view SEM micrographs showing the reference sample - glass substrate with UCNPs on the top. (With 120K magnification).

1 A.F. Oskooi, D.Roundy, M.Ibanescu, P.Bermel, J.D.Joannopoulos and S.G.Johnson, Computer Physics Communications, 20120, 181, 687-702.
2 A. Centeno, N. Alford and F. Xie, IET Nanobiotechnology, 2013, 7, 50-58.