Effect of plasmon-enhancement on photophysics in upconverting nanoparticles

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Abstract: Surface plasmon polaritons (SPP) waves have been shown to significantly affect the near-field photophysical phenomenon. In particular, strong Coulombic interactions can enhance nearby non-linear optics and energy transfer process, while SPP waves also affect other photophysical processes like quenching observed in fluorescent and excitonic systems. Here, using different plasmonic substrates, we show the effect of plasmon-enhancement on quenching, phonon-assisted non-radiative decay, weak Purcell effect or electromagnetic field enhancement, and energy transfer rates of upconverting doped-lanthanide nanoparticles. While the resonant plasmons enhance the local electromagnetic field and the rate of energy transfer leading to enhanced upconversion photoluminescence of infrared radiation to visible light, it can also increase the quenching and non-radiative decay rates of photoexcited electron-hole pairs leading to losses and lower efficiency. These results can guide the design of optimized substrate geometry for using surface plasmons to modulate the photophysics in other applications too.

OCIS codes: (100.2960) Image analysis; (190.7220) Upconversion.

References and links

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Fig. 1. (a) Energy-level diagram, upconversion excitation, and visible emission schemes for the Yb

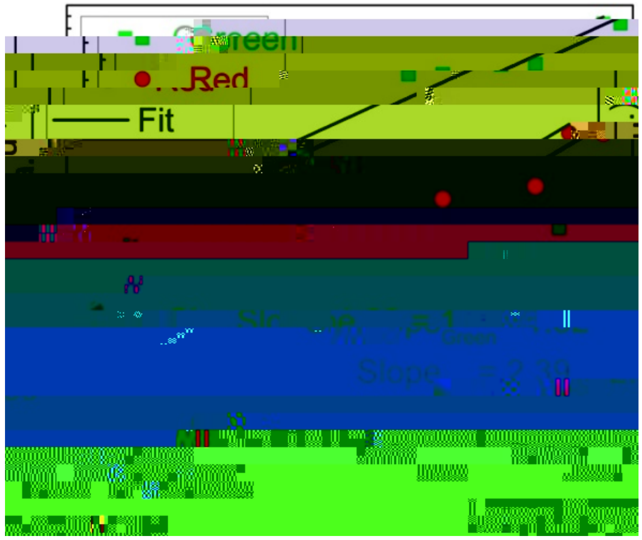

Fig. 2. Pump power dependence of upconversion emission intensities of 29 nm NaYF4:Yb^{3+}/Er^{3+} particles. The slope is ~2 which indicates two-photon process.

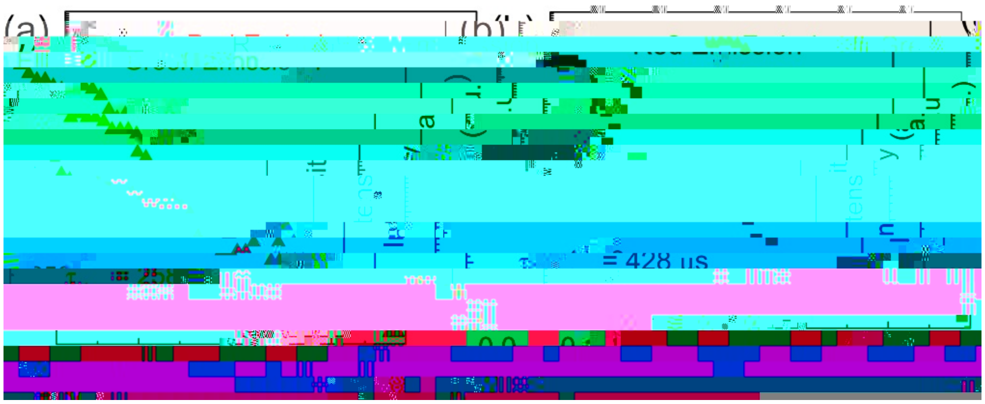

Fig. 3. Time-resolved upconversion photoluminescence (UPL) spectroscopy for (a) red and (b) green emission, respectively. The single-exponential UPL decay indicates small non-radiative relaxation from respective energy levels, and the decay times indicates respective rates of radiative decay.

#208292 - $15.00 USD Received 14 Mar 2014; revised 23 Apr 2014; accepted 23 Apr 2014; published 5 May 2014

3. Experimental results and discussions

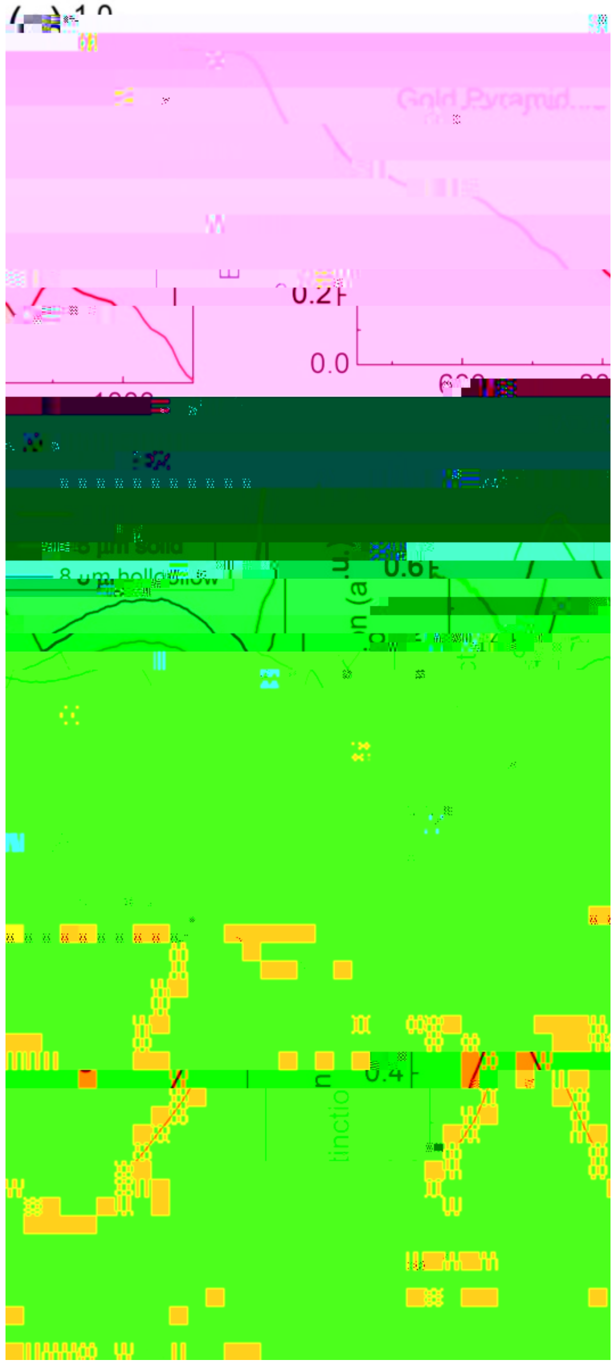

Fig. 4. Near-infrared extinction spectrum for (a) pyramid, (b) bullseye, and (c) linear grating substrates. The plasmon absorption peak shifts to lower wavelength with decreasing periodicity (as shown for bullseye in Fig. 4(b)), indicating shift of respective resonant plasmon energies.

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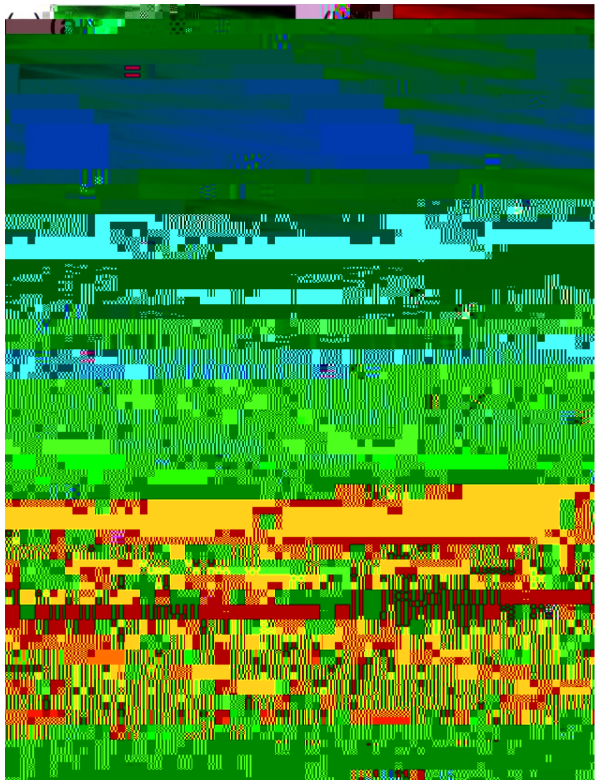


Fig. 5. (a,b) 2D confocal images for the green and red emission of 29 nm β-$NaYF_4$:Yb^{3+}/Er^{3+} particles on the linear grating substrate, respectively. (c,d) 3D confocal scan images of the green and red emission of UCNPs on the linear grating substrate, respectively. (e,f) Spatially resolved line intensity for the green and red upconversion emission on the linear grating substrate, using the 3D image.

The UCNP's (Fig. 1(b)) in films were resonantly excited (Fig. 4) on grating (Figs. 5 and 6),

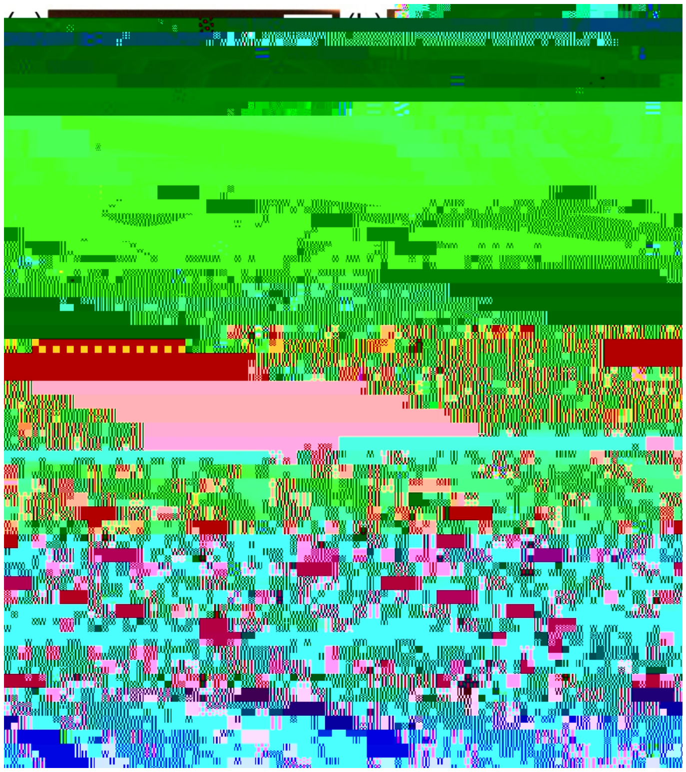
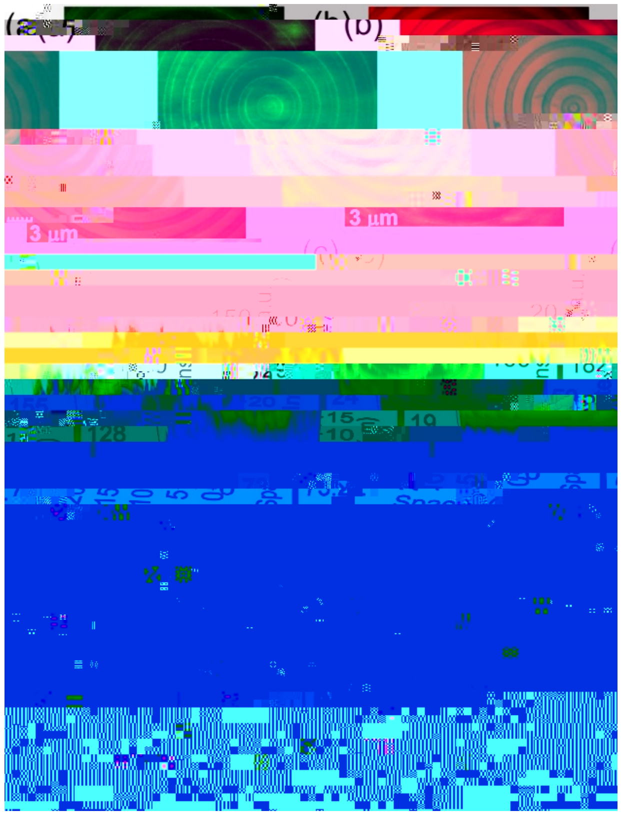
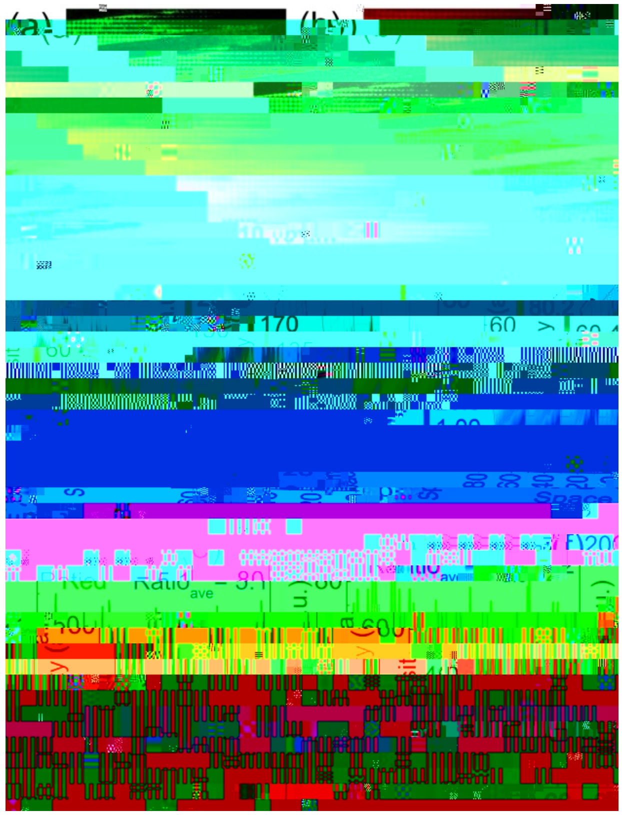


Fig. 6. Optical images of (a) linear grating, (b) bullseye, and (c) pyramid substrates. Atomic force microscopy (AFM) images of (d) linear grating, (e) bullseye, and (f) pyramid substrates. (g) AFM image of the pyramid substrate with 29 nm β-$NaYF_4$:Yb^{3+}/Er^{3+} particles. White


(a)
(b)
3 μm
3 μm


(a)
(b)

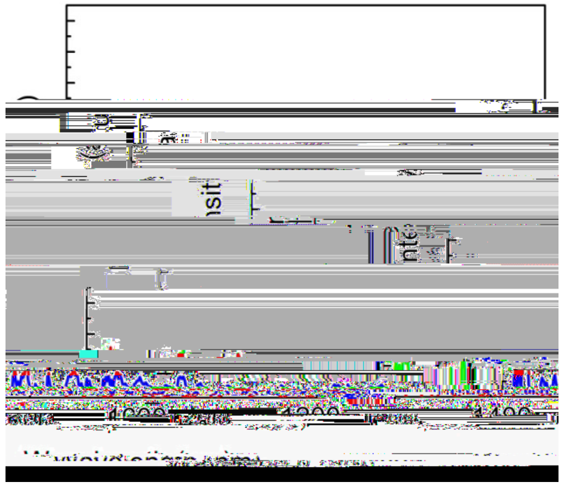


Fig. 9. Near-infrared upconversion emission spectra of 29 nm β-$NaYF_4$:17%Yb^{3+}/3%Er^{3+}

for gold substrates, the resonant energy transfer rate k_1 should be enhanced as $k_1^{'} = ak_1$, but the non-resonant energy transfer between level 0 and level 5 remains $k_3^{'} = k_3$ (the energy is far away from the plasmon resonance). The emission from level 4 on the top of substrates was given as $W'_4 N'_{Er,4tip} = W_{21} N'_{Er,2} = W_{21} \frac{k_1^{'} N_{Er} N_{Yb,1}^{'}}{k_3^{'} N_{Yb,1}^{'} + W_{21}}$. Therefore, we obtain the enhancement (top to bottom ratio) for the red emission as, $R_{red} = \frac{1.459b}{\frac{b}{a} + 0.459}$. Using the red ratio and electromagnetic enhancement (b), we obtained the energy transfer enhancement (a) of 3.2 for the linear grating, 4.3 at the center of bullseye pattern (due to plasmon nanofocusing), and the highest enhancement of 5.1 for the pyramids on a linear grating (Table 1).

While higher plasmon-enhancement in pyramids leads to very high UPL enhancements, especially for green emission (52 compared to 6.8 and 5.8 for bullseye and linear grating, Figs. 8(e), 7(e), 5(e)), the red UPL emission enhancements are more modest (5.1 compared to 2.8 and 2.7 for bullseye and linear grating, Figs. 8(f), 7(f), and 5(f)). This difference in multispectral UPL enhancement can be explained by different rates of quenching from Erbium energy levels (Table 1). Using the green UPL enhancement from UCNP's on linear grating, bullseye and pyramidal grating substrates, the emission of level 5 was given as, $_{5}\ _{Er,5}\ \frac{W_5 k_3 N_{Er,2} N_{Yb,1}}{\ _{5}\quad _{q}}$