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ARTICLE

Surface Plasmon Enhanced up-conversion from NaYF₄:Yb/Er/Gd Nano-Rods

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The surface plasmons that are enabled by grating coupling in two-dimensional gold nanoparticle arrays (AuNPAs) affected the spectral characteristics of the up-conversion (UC) emission from Yb^{3+} - Er^{3+} - Gd^{3+} co-doped sodium yttrium fluoride (NaYF₄:Yb/Er/Gd) nanorods. The red emission of NaYF₄:Yb/Er/Gd nano-rods at 660 nm (excited with a 980 nm diode laser) was significantly enhanced by the interaction with the AuNPAs. The geometric characteristics of the gold nanoparticles influenced the position of the surface plasmon resonance, and their near field strengths. The intensity of the red emission normalized versus the green emission reached 1.4, measured against a reference film in the absence of the metallic nanostructures. The lifetime for the green and red emission decreased steadily as the periodicity decreased (relative to the reference), reaching about 6% reduction for the 350 nm AuNPA. A qualitative agreement was obtained between the experimental results and finite difference time domain (FDTD) calculations.

1. Introduction

The excitation of surface plasmon resonances (SPRs) in metallic structures, ranging from individual nanoparticles to various coupled configurations, enables strong electric field confinement.^{1, 2} This strong localization is considered to be the main contribution to enhanced spectroscopic methods, such as surface-enhanced Raman scattering3,4,5 (SERS). Recently, upconversion (UC) emitters, capable of converting near infrared radiation into visible photons, have drawn much attention due to their potential for applications in a new generation of solar cells^{6, 7} and as biosensors.^{8, 9} Methods for the routine synthesis of lanthanide-doped nano-crystals have been reported.^{10, 11} These UC nano-materials, however, usually have low emission efficiency due to structural defects and large surface areas that are affected by a variety of quenchers. Previous studies demonstrated that enhanced UC efficiency may be achieved through interactions with plasmonic materials. Schietinger et al^{10} observed a strong UC emission enhancement from single Yb³⁺-Er³⁺ codoped sodium yttrium fluoride (NaYF₄:Yb³⁺/ Er³⁺) nano-crystal coupled with gold spheres. Zhang *et al*¹² reported a

five-fold overall enhancement of UC emission in NaYF₄:Yb³⁺/Er³⁺ nano-crystals in contact with gold island films. Although the interaction of UC materials with individual nano-particles and gold island films showed the potential of plasmonic to enhance the conversion efficiency, the random nature of the metallic nanostructures does not allow full control of their plasmonic properties. This lack of control on the size and shape of the metal particles, as well as the distance between the particles, makes it difficult to fully characterize the radiative decay rate and enhanced electric fields at resonance. Verhagen et al^{13} demonstrated that the UC efficiency can be tuned by organized arrangement of sub-wavelength apertures on gold films, providing insights into the role of localized and propagating plasmonic modes in the overall enhancement. Furthermore, Paudel $et al^{14}$ demonstrated that periodic plasmonic gold nanoparticle arrays (AuNPAs), designed to couple to 980 nm laser excitation, could enhance UC luminescence in the near-infrared to visible for β -NaYF₄: 17%Yb, 3%Er nano-crystals. Recently, Sun et al¹⁵ demonstrated that resonant surface plasmon polaritons (SPP) increase the rate of resonant energy transfer from Yb³⁺ to Er³⁺

ions by 6 fold on an organized pyramid gold substrate. Luu *et* al^{l6} also demonstrated SPP-enhanced infrared to visible upconversion luminescence from NaYF₄:Tm:Yb nanoparticles embedded in polymethyl methylacrylate (PMMA) supported on Au nanopillar arrays.

In this paper, we report on the controlled enhancement of UC emission from Yb³⁺-Er³⁺-Gd³⁺ co-doped sodium yttrium fluoride (NaYF4:Yb/Er/Gd) nano-rods (UC NRs) in contact with gold nano-particle arrays (AuNPAs) of various periodicities. The arrays were fabricated by electron beam lithography (EBL) on indium tin oxide (ITO)-coated glass. The plasmonic structures were specifically designed to be offresonance in the 980 nm excitation range to avoid enhanced excitation. Pure hexagonal-phase UC NRs were synthesized by a liquid-solid reaction in oleic acid and ethanol solvents.¹¹ Thin films of UC NRs were directly spin coated on the AuNPAs. It is shown that the emission from UC NRs is enhanced by the AuNPAs, and that the relative magnitude of the enhancement in the green and red regions was controlled by the varying periodicity of the arrays. It is also demonstrated experimentally and numerically that SPR assisted diffractive coupling in 2D AuNPAs contributes to the overall enhancement of UC emission.

2. Experimental Section

2.1 Substrate fabrication: AuNPAs on ITO-coated glass

AuNPAs with different periodicities were fabricated by electron beam lithography (EBL). In general, an electron-resist, 6 % PMMA (polymethyl methacrylate) was spin-coated (4000 rpm) on the surface of indium-tin oxide (120 nm ITO) coated glass slide and then exposed to an electron beam that defined a previously set of regular nano-hole patterns. 2 sets of 7 square arrays, 100 x 100 μ m² for each periodicity, were fabricated in a given sample. The arrays periodicities ranged from 350 nm to 550 nm and each individual array was separated by 200 µm (Figure 1d). After development of the PMMA resist, 100 nm of Au (a 5 nm Cr layer was deposited first for adhesion) was ebeam evaporated onto the pattern. Finally, a "lift-off" procedure was implemented to remove the mask, resulting in the designed AuNPAs (Figure 1a and b). The diameter of each Au NP in the arrays was ~ 130 nm, the height was 100 nm (e-beam evaporated). The ITO-coated glass substrate was used because of its excellent transparency (84%) in the visible range and its good conductivity (sheet resistance: $8 \sim 12 \ \Omega/cm^2$) for the EBL process. The ITO substrate was purchased from Sigma-Aldrich and cleaned in acetone, ethanol, isopropanol and deionized water in a sonicator for 5 minutes each, respectively. The samples were nitrogen blown dried before use.

2.2 UC material: NaYF₄:Yb/Er/Gd NRs

 $NaYF_4:Yb/Er/Gd$ NRs were synthesized according to the procedures described elsewhere.¹¹ Basically, a 1.5 g NaOH in de-ionized water solution (7.5 mL) was mixed with 25 mL of ethanol and 25 mL of oleic acid under stirring. 2 mL of RECl₃

(0.2 M, RE=Y, Yb, Er and Gd, YCl₃:YbCl₃:ErCl₃:GdCl₃ =50:18:2:30 mol%) solution and 1 mL of NH₄F (2 M) was added to the resulting mixture. The solution was transferred into a 100 mL of Teflon-lined autoclave and heated at 200 °C for 2 hours to obtain the UC NRs. Then, the UC NRs were washed several times with de-ionized water and ethanol by centrifugation.

In order to obtain uniform surface coverages, the UC NRs were concentrated five times from the original stock suspensions before being used to coat the substrates containing the AuNPAs. The UC NRs were then spin-coated onto the AuNPAs at 1000 rpm in ethanol. It was extremely challenging to obtain uniform AuNRs films, and 350 nm was the minimum thickness that allowed a homogeneous coating by spin coating. Scanning electron micrographs (SEM) images of UC NRs coated AuNPA substrate are presented in Figure 1c and optical image is presented in Figure 1d.



Figure 1 (a) SEM top view of an AuNPA (420 nm periodicity), and (b) Side view of AuNPs (substrate titled at 45°) on ITO glass substrate (c) UC NRs film covering AuNPAs in a large area (substrate titled at 60°) and the close view of the UC NRs film (the inserted SEM also viewed at 60° tilt) (d) Optical microscope images of a UC NRs film covered AuNPAs, each array shows difference color under white light illumination at a titled angle; The numbers indicates the periodicities of each array; the inserted image shows one UC NRs film covered array under a higher magnification (50X objective). Dimensions: scale bars (a) and (b) 200 nm; (c) 20 μ m and 200 nm on the whole surface and inserted SEM, respectively; (d) 100 x 100 μ m² for each AuNPA square.

2.3 Characterization of UC NRs coated AuNPAs ITO substrate

The transmittance/extinction experiments for UC film covered AuNPAs were carried out using a fiber (400 μ m core diameter) coupled optical microscope (OLYMPUS MS PLAN ULWD 50X, NA 0.55 objective) and a UV/VIS/NIR spectrometer (Ocean Optics 4000) as a detection system. The emission spectra were obtained under 980 nm continuous wave laser excitation with a fixed power density of 200 W/cm². The illumination area was about 0.05 mm² within each square AuNPA (shown in Figure 3a). The laser beam was incident normally onto the UC covered AuNPAs sample, then, the UC emission was collected at the back of sample with a spectrograph (HoloSpec VPT System) coupled to a CCD camera (ANDOR Technology). The experimental setup is

illustrated in the supplemental information (SI, Figure SI-1a) file. The emission lifetimes for the UC film covered AuNPAs and references were measured, the experimental setup is illustrated in the SI-1b. SEM images were taken using a scanning electron microscope Hitachi S4800 at 1KV acceleration voltage.

2.4 FDTD simulations

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The FDTD simulations were performed using the Lumerical software housed at WestGrid (Western Canada Research Grid, part of Compute Canada national consortia for high performance computing). The diameter of Au NP was set at 130 nm, and the height was 100 nm. Au NP model was based on the average measurements from the SEM images. The Au NP was placed on an ITO (120 nm) glass with 5 nm Cr (as the adhesion layer) between Au NP and ITO, and the nanostructures were buried in a 350 nm dielectric film. The UC NR film refractive index (n) was set as 1.2 (which was less than 1.50 for the NaYF₄ crystal,¹⁷ by taking into consideration the smaller packing density of UC NRs than the NaYF₄ crystal), 1.65 for the ITO film and 1.45 for the glass substrate. The dielectric properties of the gold were the data reported by Cooperative Research Centres (CRC) and used directly from the Lumerical material data base. Periodic boundary conditions were used in each periodicity for xy direction and with PML (perfect metal layers) in the z directions. Plane wave source was placed 500 nm above ITO surface assuming that UC emission was random inside the UC NR film; the light travelling to the detector z direction was collected.

3. Result and Discussion

Square arrays of gold nanoparticles (AuNPAs) with different periodicities were fabricated by EBL. The periodicity, corresponding to the distance between the Au NPs, ranged from 350 nm to 550 nm, while the base diameter of NPs was measured nearly constant at 130 nm. The height (thickness) of all Au NPs was 100 nm (e-beam evaporated). Each array occupied a square region of 100 x 100 µm² (Figures 1d). Figures 1 (a) and (b) show the SEM images of a 420 nm period AuNPA (top view (Figure 1a) and side view (Figure 1b, tilted at 45°)) before the deposition of UC NRs. UC NRs were synthesized according to the procedures described in reference.¹¹ A layer (~350 nm thick estimated from the SEM images of UC NRs film edge) of NaYF4:Yb/Er/Gd nano-rods (UC NRs) was deposited on the surface of the AuNPAs by spin coating (1000 rpm in ethanol). Figure 1c shows the SEM surface topology (tilted at 60°) of the multi-layers UC NRs covering the AuNPAs in the substrate. The SEM image also in Figure 1c indicates a relative homogenous coverage with a random UC NRs packing (the multi-layers of UC NRs is referred as the "UC NRs film" in the following discussion). The individual UC NRs were about 400 nm long and 40 nm wide, in general, as shown in the inserted SEM image in Figure 1c. Figure 1d presents the optical image of an UC NRs film covered AuNPAs of different periodicities, illuminated by

white light at a tilted angle ($\sim 30^{\circ}$). The observed different color of the each array correlates to the grating diffraction of the AuNPAs at different periodicity (as indicated).



Figure 2 (a) Normalized extinction spectra of the UC NRs film coated AuNPAs (from 350 nm to 450 nm periodicity), calculated from the experimental transmittance spectra. UC emission spectrum is shown as an insert (orange color) for comparison. The laser excitation wavelength was at 980 nm (indicated as a vertical line). (b) FDTD calculated extinction spectra as a function of the grating constant of AuNPAs in a dielectric NaYF₄ film (n=1.2) on the ITO (n=1.65) glass substrate (detailed simulation information see the method section).

Before measuring UC NRs film emissions, the extinction spectra were measured from the AuNPAs coated with UC NRs films. The experimental extinction cross sections (σ_{ext}) of AuNPAs of different periodicities, ranging from 350 nm to 450 nm, coated with UC NRs film, are presented in figure 2a (500 nm and 550 nm periodicities are presented in SI: Figure SI-2). The number of particles contributing to the extinction crosssection depends on the periodicity and this difference in particle separations were taken into account.¹⁸ A reference UC emission spectrum (UC NRs film on ITO-coated glass) is also shown in figure 2a for comparison (orange color). It can be seen from Figure 2a that the "green" (between 520 nm to 570 nm) and the "red" (and 640 nm to 690 nm) UC emissions present different degrees of overlapping with the surface-plasmon resonances (SPRs) from each AuNPA. The positions of the SPRs (peaks in the AuNPAs extinction spectra) were tuned by the periodicities of the arrays. It is well known that when metallic NPs are arranged into periodic arrays, their SPR can be modified due to

electromagnetic coupling between the particles.^{19, 20} The local electrical field in a periodic array of nanoparticles is expected to be larger than for individual nanoparticle, due to this coupling effect.²⁰ A plane wave source (wavelength ranging from 400 nm to 1000 nm) was used to simulate the electrical field at the surface of AuNPAs coated by an UC film on ITO substrate. Although the FDTD simulations of the extinction cross section, Figure 2b, do not match the experimental data (shown in Figure 2a) exactly due to several factors: including the nature of fabrication defects, ITO and Au NPs surface roughness, the packing density of solid UC NRs film, etc., the general trend and peak positions obtained numerically from FDTD (Figure 2b) qualitatively agrees with the experimental results (Figure 2a). The broad resonance peaks in Figures 2a and 2b can be assigned to SPR assisted by diffractive modes. The SPR in metallic periodic structures can be excited when the Bragg condition is satisfied.²¹ This type of diffractive coupling has been widely observed in arrays of nanoparticles²²⁻²⁵ and nanoholes.²⁶⁻²⁸ The SPR red shifts as the periodicity of the arrays increases as shown in both the experimental and the simulation results (Figure 2a and Figure 2b, respectively). The shape of the SPR bands has some dependence on the experimental configuration. For instance, when a high NA lens is used in the collection, high order diffraction modes can contribute to the overall shape. In our experiments, a low NA (0.22) optical fiber was used. The fiber was positioned to ensure that mostly the normal component of the transmission was collected.

Figure 3a illustrates the experimental arrangement for the UC NRs emission measurements. The 980nm laser was used to excite the UC NRs film at the top the AuNPAs, and the emission spectra from the UC NRs film were collected at the bottom of the ITO glass substrate. The insets in Figure 3a are optical images of the UC emission under 980 nm laser excitation from both an AuNPA and a bare ITO (reference) covered with UC NRs film. The emission from the reference (ITO glass substrate covered with UC NRs film but in the absence of the Au nanostructure) is always taken near (~200 µm apart) the AuNPAs of interest on the same substrate, as shown in figure 3a. Figure 3b presents an example of emission spectra obtained from the UC NRs film on AuNPAs with different periodicities. A reference spectrum was also included to illustrate the emission enhancement due to the presence of the plasmonic structures. As seen in Figure 3b, the UC material exhibited green emissions centered at 530 nm and 550 nm, assigned to the ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transitions from Er³⁺ ions, respectively, and a red emission, centered at 667 nm, associated with the ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2} \text{ Er}^{3+}$ transition.¹¹ The relative intensities between the red and green emissions changed with the array periodicity and were different than the reference. The integrated UC luminescence, green and red intensity for one set of AuNPAs, were further evaluated and plotted in Figure 3c. Green and red represent the combined emissions in both regions, 520 nm to 570 nm and 640 nm to 690 nm, respectively. All samples were measured in triplicates and a small variation in the intensities (less than 10%) was found between different

measurements. The UC emission in Figure 3c vary strongly with the array periodicities and this effect is much more pronounced for the red than for the green emission. The largest UC enhancement in Figure 3c, of about 2 times, was observed for the red emission from an AuNPA with a 420 nm periodicity. A wide range of integrated UC emission intensity enhancements (ranging from less than 10 to several hundreds) has been reported throughout the plasmonic literature^{15, 16, 29-31}. The maximum of ~2 times enhancement, observed in Fig. 3c, is at the low-end compared to reports from other groups, maybe because the structures studied here were designed to avoid plasmonic enhancement at the laser excitation wavelength.³⁰

In order to quantify the tunable preferential enhancement, the relative integrated area intensity between the red and the green emission $(I_{Red}^{AuNPA}/I_{Green}^{AuNPA})$ were calculated, and plotted versus the periodicity in figure 3d. The reference $(I_{Red}^{0}/I_{Green}^{0})$ in the absence of an AuNPA is included in Figure 3d. The peak area ratio $I_{Red}^{AuNPA}/I_{Green}^{AuNPA}$ for the AuNPA with 350 nm periodicities was about 1.38, while the integrated peak area ratio $I_{Red}^{0}/I_{Green}^{0}$ for the reference as the periodicity of the reference sample was about 0.98. The preferential enhancement of the red emission decreased as the periodicity of the AuNPAs increased (Figure 3d). A similar trend was observed for another set of AuNPAs (350 nm to 550 nm periodicity) separated by 500 µm from the first set and fabricated on the same substrate. The error bars in figure 3d represent the variation between these two data sets.

Figure 3 summarizes the two main findings of this work: (1) tunable enhancement in the up-conversion emission for UC NR film in contact to the AuNPAs relative to UC films reference on bare ITO substrate; (2) the dependence of the characteristics (red/green intensity ratios) of this enhancement with the geometric parameters of the arrays.



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Figure 3 (a) Schematic of the UC measurement setup, the inserts are showing the optical images of UC emission under 980 nm laser excitation from an AuNPA (each array are separated by 200 μ m apart as shown in figure 1d) and the reference (in the absence of the Au nanostructure) that is taken near (~200 μ m away) the AuNPAs on the same ITO substrate as shown. **(b)** A sample of UC emission spectra from AuNPAs coated with UC NRs and a reference near the AuNPAs for comparison. The different periodicities are indicated in the figure 2b. Assignments for the electronic transitions are also shown. **(c)** The integrated peak area green (from 520 nm to 570 nm) and red (from 640 nm to 690 nm) UC emission intensities in contact to AuNPAs with different periodicities are presented. **(d)** Relative integrated intensity between the red and the green emission (I^{AuNPA}/I^{AuNPA}) with different periodicities are presented, the

reference (red color point) is included as (I^0_{Red}/I^0_{Green}) in absence of AuNPA on the same ITO-coated glass substrate, the error bars represent the variation between the two series of AuNPA sets.

Plasmonic-mediated enhanced emissions are often due to an enhancement of local electric fields and to an increase of the radiative decay rate.^{16, 31} In the particular case of the structures investigated in this work, the SPR of the nanostructures is not in resonance with the experimental excitation at 980 nm (note the laser excitation energy indicated as a vertical line in Figure 2a). The trend of the preferential enhancement of the red emission relative to the green emission (presented in Figure 3d) can be justified by considering the relative overlap with the local electrical field strengths at those emissions for different array periodicities. Notice that, although different relative UC enhancements for the red and green emissions are often observed, ^{15, 30, 31} our geometric variations allowed tuning to the ($I_{Red}^{AUNPA}/I_{Green}^{AUNPA}$)-ratio.

The UC Er³⁺ emission is a random dipole emission, as for the UC NRs close to the AuNPAs, the dipole emission will significantly depend on the position and distance away from the Au NPs.³² However, since the UC film on top of the AuNPA is relatively thick (~350 nm) and only the light travelling to the bottom detector is collected, UC film emission were considered as a collective plane wave source travelling towards to the AuNPAs. The exact number and position of UC emitters inside the plasmonic field is not easy to estimate with good precision due to several factors, including that the extension of the field changes with the wavelength. The experiments then measured a statistic average of the UC emission considering all the collective emitters (inside and outside the field). The minimum spatial extent of the plasmonic fields, estimated by FDTD, is about 20 nm. In this limit, most of the field contribution is restricted to a distance within the first layer of UC NRs. This field decays exponentially towards the film). This means that only about 10% of the emitters in the film should be responsible to the bulk of the enhanced UC generation within this approximation.





Figure 4 (a) FDTD calculated maximum electric near field intensity $|E|^2$ (contour colour plot), between 450 nm to 1000 nm wavelength light (y-axis), for different AuNPA periodicities (x-axis) are presented. The field was calculated adjacent to the gold surface. **(b)** FDTD calculated relative near field intensity $(I_{Red}^{AuNPA}/I_{Green}^{AuNPA})$, integrated between the red and green light (as indicated in the figure 4a) with different AuNPA periodicity is presented.

FDTD calculated local electric field intensity contour profiles are presented in Figure 4a from the plane wave source simulation. Figure 4a (the contour plot) shows the maximum field promoted by the Au NPs for each periodicity in the 450 nm to 1000 nm spectral range. The regions that corresponding with the UC NRs emissions are outlined by dashed lines in Figure 4a. Due to the complicated nature of the system investigated here, a quantitative matching between the FDTD calculation local electrical field intensity and the experimentally measured UC emissions is challenging; however, the calculation qualitatively follows the experimental trend, since the local electrical field intensity in the red emission region was always larger than the local electric field in the green emission region. Moreover, the local electrical field intensity in the red emission region was more sensitive to AuNPA periodicity variations (Figure 4a) than its green emission counterpart. Figures 4b presents the FDTD calculated relative electric near-field intensity profiles (in the xz plane at green (from 520 nm to 570 nm) and red (from 640 nm to 690 nm) from Figure 4a. The profile in figure 4b shows a trend where the UC-enhanced emissions were tuned by the local SPR field at the emission wavelengths. This FDTD calculated trend (Figure 4b) qualitatively follows the experimental measured trend presented in Figure 3d. Hence, the relative enhanced red/green UC emission depends strongly on its degree of overlap with the near electric field intensity. A preferential decay channel opens when the emission energies (from the UC material) overlap with the plasmonic resonances of the AuNPA. This should increase the decay rate, as the energy of the emitter may be directly transferred to the plasmon mode.33, 34

However, the light emission can be recovered from the plasmon decay, leading to an increase in the flux of photons produced by the system. This enhancement mechanism can then be characterized by a decrease in the emitter's lifetime due to the presence of the AuNPA.



Figure 5 Decay lifetimes measured from monochromatic green (from 520 nm to 570 nm) and red (from 640 nm to 690 nm) UC light emission, respectively, from 350 nm to 450 nm AuNPAs and reference (on the same ITO-coated glass substrate).

Excited state lifetimes for the up-conversion luminescence of UC NR films on either AuNPAs (periodicity from 350 nm to 450 nm) and references (UC NRs film on the same ITO substrate in absent of AuNPA) were measured using a photomultiplier tube coupled to a microscope (experimental details in the SI, Figure SI-1b and Figure SI-3). The lifetime results are summarized in Figure 5. UC NRs showed different lifetime decays for the green (520 nm to 570 nm, ~200 µs) and red (640 nm to 690 nm, ~350 µs) emissions. The lifetime of the UC material in contact to the plasmonic structure was altered for both green and red emissions. The lifetime for the green and red emission decreased steadily as the periodicity decreased (relative to the reference as shown in Figure 5), reaching about 6% reduction for the 350 nm AuNPA. The plasmonic enhancement effect on the emission of the UC NRs is expected to be correlated to the reduced lifetime decay, but the 420 nmperiodicity array was the one that presented the maximum enhanced emission from the set (Figure 2). Moreover, the lifetimes in figure 5 do not seem to depend significantly on the periodicities. Optical resonances enhance the radiative rate and introduces additional non-radiative decay channels,¹⁰ leading to decreased lifetimes, and increased quantum yields.35, 36,37 However, the effect of the optical mode within the emitter's environment is also a very important parameter. For instance, Schietinger¹⁰ demonstrated that the UC decay lifetime is affected significantly by the position of a emitter (a single NaYF₄ nanocrystal codoped with Yb³⁺/ Er^{3+}) in between two Au nanoparticles. The magnitude of the plasmonic quenching and lifetime decay presented in our experiment (6%), however, was much lower than other reported results (~50% for Ag nanostructures, for example) in the literature.^{10, 38-40} On the other hand, there are examples in the literature of much smaller effect of Au nanostructures on the emission lifetime than generally observed for Ag^{10, 38-40} and even cases of lifetime increase.^{40, 41} In any case, the modest decrease in the lifetime emission due to

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the plasmonic structure was a surprising result, since the FDTD simulations presented in Figure 4 pointed towards an enhancement mechanism that involves preferential decay into the SPR modes. One possible explanation for the small lifetime reduction could take into consideration the relatively thick UC film with large "empty" spaces between individual Au NPs; therefore, the measured statistical lifetimes would have contributions from the emitters in different parts of the film that interact with the SPR field at various levels depending on their positions (even though the emitters closer to the gold surface are expected to experience the stronger fields).⁴² The effect of this emission interference from the bulk UC emission decay is to increase the measured average lifetime, relative to what has been observed in the literature.^{35, 36}

Although the results presented in Figures 2 - 4 suggested that the regular plasmonic channels plays a major role in the luminescence enhancement, the modest variation in lifetime and the fact that the maximum enhancement does not coincide with the minimum lifetime prompted us to also consider other grating-mediated mechanisms that are not expected to significantly affect the lifetime. For instance, for grating spacing less than the light wavelength, the zeroth grating order scatter (forward scattering) is expected to be enhanced.43, 44 The FDTD calculated far-field profiles (Figure SI-4) indicates that AuNPA also exhibited different degree of collimation and directional effect for green and red emissions. This increase in the directionality of the emission to the forward direction could affect how much light is scattered into the collection objective, but it is not expected to significantly change the UC lifetime (one can imagine the metallic grating as a mirror that preferentially scatters into the detection system). The directional scattering was observed for all periodicities and agrees with the literature.^{45, 46} Thus, the relative enhancement could be also influenced by how much light can be redirected to the forward direction from a particular wavelength. The FDTD calculations (Fig. SI-4), however, indicated a better collimation for the green emission, which is contrary to our experimental observations. Temperature effects, caused by laser heating, should also be considered. In fact, if the temperature deviates significantly from the room temperature, it could also affect the Er³⁺ emission intensity.^{47, 48} However, the relative intensities of the green emission from the thermally connected ${}^{2}H_{11/2}$ and ${}^{4}S_{3/2}$ states indicate that laser heating is not significant.49

All these arguments, together with the observation of good overlapping between the red emission and the extinction SPR band (Figure 2) and dipole plasmon model (FDTD calculation, Figure 4), suggest strongly that surface plasmons excitations play a significant role in the emission enhancement effects. However, other factors may also contribute (or compete) to the plasmonic effect. For instance, the decrease in the UC enhancement for periodicities smaller than 420 nm might not have contributions only from the plasmonic effect (notice the decrease in calculated local field intensities at the emission wavelengths for small periodicities in Fig. 4a), but also from an increase in reflectivity due to a higher density of Au NPs (which decreases the forward scattering). In summary, the relative enhancement of the UC emission in contact to AuNPAs on ITO could be controlled by several contributions that depend on the diffractive characteristics of the structure. These include the near-field contributions; temperature variations; and the increased directionality of the scattering. However, our analysis seems to indicate that the plasmonic near field overlap with the emission is still the main driving force for the enhanced UC. This allows the emission of UC NRs to be controlled by the geometric parameters of the gold nanostructures.

4. Conclusions

The enhancement of UC emission through plasmonic interactions between NaYF4:Yb/Er/Gd nanorods and AuNPAs with various periodicities was investigated. A maximum ~2 times enhancement in UC emission was obtained for an AuNPA with periodicity equals to 420 nm via the coupling of the Er³⁺ red transition to the SPRs modes of the AuNPA. This enhancement, however, was mainly generated by the NRs in closer contact to the gold film and might correspond to contributions from only about 10% of the total emitters (estimated upper limit for the enhancement). The preferential enhancement of the red emission qualitatively agreed with the local near field trend predicted by FDTD simulations. The observed effect of the decrease in the lifetime of the UC emitter suggest that radiationless quenching of the emission into SPR following by emission from the plasmonic modes, nanostructure might be the preferred channel for the enhancement. Other possibilities, such as increased directionality and temperature effects, were also considered. We believe that these results offer new insights into the control of plasmonic-excitation-emission interaction, which should help provide new routes to rationally modulate up-conversion emissions in the future.

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[†] Electronic Supplementary Information (ESI) available: Experiment setup details, extinction spectra, decay lifetime measurement and far field profiles as mention in the text. See DOI: 10.1039/b000000x/

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Journal Name

Table of Contents Graphic



Brief Summary

The enhancement of upconversion emission from Yb^{3+} - Er^{3+} - Gd^{3+} co-doped sodium yttrium fluoride (NaYF₄:Yb/Er/Gd) nano-rods (UC NRs) was controlled by gold nanoparticle arrays (AuNPAs) of various periodicities.