Large Enhancement of Upconversion Luminescence of NaYF₄:Yb³⁺/Er³⁺ Nanocrystal by 3D Plasmonic Nano-Antennas

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We investigated the enhancement of the upconversion luminescence (UCL) of NaYF₄:Yb³⁺/Er³⁺ co-doped nanocrystals using a 3D plasmonic nanoantenna architecture: disk-coupled dots-on-pillar antenna array (D2PA). By optimizing the D2PA structure, we observed a 310-fold UCL enhancement uniformly over a large area and an 8-fold reduction in the luminescence decay time. The enhancement factor is two orders of magnitude larger than the previously reported results on the same type UCL material.[3]

Upconversion luminescence is a nonlinear process which re-emits a photon at a shorter wavelength by absorbing more than one photon successively at longer wavelengths via long-lived intermediate energy states of a UCL material.[4] Unlike other nonlinear frequency upconversion effects, e.g., second harmonic generation, which requires a high pumping intensity that often has to be achieved by expensive and bulky pulsed lasers, the UCL can be excited by low power cw lasers, and even by non-coherent light sources,[5] opening the door for many important applications in various fields, such as life sciences,[4–6] medicine,[7] display,[8] laser,[9,10] and solar energy.[11]

Driven by the potential applications, enormous endeavors have been made to develop new UCL materials, particularly, materials based on lanthanide ions such as Tm³⁺, Ho³⁺, and Er³⁺, which offer long-lived intermediate energy states, ideal for the UCL.[12] In this trend, many researches have been focused on optimizing the host materials, and significant signal improvements have been reported via different approaches, such as tuning the size of host particles, depressing unwanted phonon effects, and reducing the quenching induced by surface effects.[13–17] Meanwhile, another line of research has been focused on improving the light collection efficiency of the lanthanide ions with sensitizers, a material exhibiting strong light absorption at the wavelengths which match the intermediate energy levels of the upconverting lanthanide ions. Today, one of the most efficient lanthanide-ion-based UCL materials is the Er³⁺ doped hexagonal phase NaYF₄ crystal sensitized by Yb³⁺ ions (i.e., the Yb³⁺ ions collect the pumping light and transfer the energy to Er³⁺ ions, which then upconvert photon energy via the lone-lived ladder-form energy levels).[18–22] In this energy transfer (ET) process, the UCL efficiency depends on the light collection efficiency of the sensitizers (i.e., Yb³⁺ ions); it is therefore possible to improve the UCL efficiency by using metal nanostructures, which can further enhance the optical absorption cross-section of the sensitizers.

It is well known that metal nanostructures (i.e. plasmon substrates) can efficiently collect light and enhance the light intensity in their vicinity due to surface plasmon resonances, and these effects have been widely used for enhancing various optical processes, such as the Raman scattering,[23] downconversion luminescence,[24] and upconversion luminescence.[25–29] However, for NaYF₄: Yb³⁺/Er³⁺ nanocrystals, previous reported enhancements were less than 5 times,[30] and in some cases, people even saw quenching instead of enhancement.[30] This is due to the following reasons: (1) the unoptimized design of the substrate, (2) frequency mismatch between the plasmon resonance and the pumping light, and (3) quenching effect caused by the metal. In addition to the low enhancement factor, currently, it is still challenging to fabricate a high performance nanostructured metal substrate over a large area with a low cost. This also hinders the plasmon-enhanced UCL (PEUCL) from being implemented in real-world applications.

To overcome the issues mentioned above, in this work, we utilize a novel 3D plasmonic architecture, the disk-coupled dots-on-pillar antenna array, to enhance the UCL of NaYF₄: Yb³⁺/Er³⁺ co-doped nanocrystals (Figure 1a). The D2PA structure is a 3D nanocavity array composed of Au nanodisks on the top of periodic dielectric pillars, an Au backplane at the feet of the pillars, and dense Au nanodots on the sidewalls, Figure 1b.[31] The Au nanodisks and Au backplane confine the light both vertically and laterally. They collect and funnel the light into the cavity areas, and create a large electric field enhancement in the nanogaps. Compared with the previously reported structures, the D2PA structure packs a large number of “hot spots” with a high density, and a great uniformity over the wafer scale, making it an ideal structure for the plasmon-enhanced spectroscopy. Of equal significance is the novel nanofabrication method for D2PA, which combines nanoimprint, self-assembly, and self-alignment, and fabricates the 3D plasmonic nanostructures over a large area, precisely, uniformly, and cost-effectively. Indeed, using the D2PA, we have recently achieved a very large enhancement for Raman scattering (>10⁹ x).[31] However, the plasmon-enhanced UCL is very different from the surface-enhanced Raman scattering due to the sophisticated coupling mechanisms between the plasmon resonance modes and energy levels of the lanthanide ions. In this work, we present a systematic study of plasmon-enhanced UCL on D2PAs with...
different geometrical parameters, as well as the associated decay rate enhancement of UCL. 

**D2PA Substrate Fabrication:** The D2PA substrates were fabricated by the nanoimprint method, which allows us to make mass production of nanostructures with a sub-10 nm precision at the wafer scale. In brief, SiO\(_2\) nanopillars were first patterned with nanoimprint and reactive ion etching (RIE), and then Au nanodisks, backplane, and nanodots on the nanopillar sidewall were all formed within one step of Au evaporation (Detailed fabrication has been published elsewhere). Many structural parameters that affect the resonance properties of the D2PA can be controlled and tuned precisely in the fabrication. Particularly, we focused on the pillar height of D2PA in this work, since it determines the size of Au nano-disk-backplane gap where the electric field is mostly confined and enhanced, similar to the case of the conventional laterally aligned antennas, such as bow-tie and dipole antennas. More detailedly, we varied the height of the SiO\(_2\) pillars by controlling the RIE time.

Hexagonal-phase NaYF\(_4\):Yb\(^{3+}\)/Er\(^{3+}\) nanocrystals (18\% Yb\(^{3+}\), 2\% Er\(^{3+}\), 25 nm in diameter, 10 mg/mL in hexane, Sun Innovation Inc.) were used in this work. The nanocrystal solution was diluted by 10 times in hexane and then was spin-coated on the D2PA substrate (4000 rpm for 1 min), resulting in a submonolayer coverage with an average area density of \(\sim 200 \mu m^{-2}\). Most of the nanocrystals were attached on the side wall of the glass pillars and Au nanodisks, as shown in Figure 1c. NaYF\(_4\):Yb\(^{3+}\)/Er\(^{3+}\) nanocrystals were spin-coated under the same condition onto a glass substrate as a reference in this work, Figure 1d. The nanocrystals formed discontinuous submicrometer islands on the substrate, which were uniform at a scale >10 \(\mu m\). We characterized the densities of nanocrystal using SEM pictures, and found that the average area density was about 900 \(\mu m^{-2}\) on the reference substrate, 4.5 times of the nanocrystal density on the D2PA substrate.

The UCL was characterized using a homebuilt optical system (Figure 1e). A 980 nm cw laser was used as the pumping source (Laserglow Technologies Inc.), and the pumping power can be continuously tuned by a variable attenuator and monitored by a power meter (Model 1830-c, Newport). The pumping laser was focused on the samples with a spot size of \(\sim 1,000 \mu m^2\), and the excited UCL was then collected and coupled into a multimode fiber, which guided the luminescence signal into a spectrograph (LabRaman Aramis, Horiba). The same setup was also used for the time-resolved measurements, in which the laser beam was modulated by a chopper to generate square pulses, and the UCL signals were detected by a photomultiplier tube and recorded by an oscilloscope.

**Optimizing D2PA Structure for Plasmon-Enhanced Upconversion:** We first optimized the enhancement of the upconversion luminescence by changing the height of the SiO\(_2\) pillars, \(h\), which determines the coupling strength of the D2PA’s metal disk with the metal backplane, and six different pillar heights (50 nm, 58 nm, 67 nm, 75 nm, 83 nm, and 100 nm) were produced with different etching times. Other parameters were fixed (200 nm pitch size, 50 nm Au deposition, and 100 nm pillar diameter) in the process. The resulted D2PA structures were carefully characterized using SEM, as shown in Figure 2a,b.

The enhanced UCL spectra were measured on both the D2PA substrates and the reference substrate, with a 3 mW pumping power, \(\sim 1,000 \mu m^2\) focus spot (i.e., \(3 \times 10^2 W/cm^2\)), and 1 s collection time. The UCL spectra were collected from six randomly chosen areas on each sample, and their deviations were less than 10% over the whole sample. This small variation in UCL signals implies that both the D2PA substrates and the nanocrystals were uniform over a large area.
conditions, as shown in Figure 3a. The enhancement factor for each luminescence peak is determined by:

$$S_{up} \propto P_{n, pump}$$

Where $S_{D2PA}$ and $S_{ref}$ is the UCL intensity, and $N_{D2PA}$ and $N_{ref}$ is the area density of the NaYF$_4$:Yb$^{3+}$/Er$^{3+}$-codoped nanocrystals, on the D2PA and the reference substrate, respectively. The $N_{D2PA}$ and $N_{ref}$ were obtained by carefully counting the particle numbers on high resolution SEM images. For $N_{D2PA} = 200$ particle/$\mu$m$^2$, and $N_{ref} = 900$ particle/$\mu$m$^2$, the enhancement factor was 310-fold and 100-fold for the peak at 660 nm and the peak at 550 nm, respectively. This value is 2 orders of magnitude larger than the previously reported results on the same type of nanocrystals. [1, 30]

This large enhancement can be directly visualized with luminescence photography, as shown in Figure 3b–d. Both the D2PA

Figure 2. Pillar height effect of D2PA structure on UCL. (a) and (b) show the SEM images of D2PAs with different pillar heights (50 nm and 100 nm, respectively). (c) UCL intensity vs. pillar height for the luminescence peaks at ~550 nm and ~660 nm, respectively. The inset depicts a typical UCL spectrum, and the integrated intensities of the UCL peaks (over the shadowed areas) were used in (c). (d) Measured reflection spectra of D2PA substrates with different pillar heights.

The measured UCL spectrum exhibits two major groups of peaks, which are located at ~550 nm and 660 nm (inset in Figure 2c), and corresponding to the transition of $^4H_{11/2}/^4S_{3/2} - ^4I_{15/2}$, and $^4I_{9/2} - ^4F_{15/2}$, respectively. We plot the intensities of these two groups of peaks (which are defined as the integral over the marked spectral areas in the inset of Figure 2c) as functions of the pillar height, and find that the enhancement factor of the UCL signal is strongly related to the pillar height, as depicted in Figure 2c. When pillar height $h$ is 50 nm, the intensity of peak 2 (660 nm) is low, the signal intensity increases and reaches the maximum when $h$ increases from 50 nm to 75 nm, and then, the UCL signal starts to drop when $h$ is further increased. Same phenomenon was also observed for the peaks at ~550 nm.

In order to explain this pillar height dependent luminescence enhancement, we measured the reflection spectra of the D2PA substrates, as shown Figure 2d. Significant resonance shifts were observed when $h$ varied. When the pillar height is large (100 nm), resonance absorption (the dip in the curve) appears at ~850 nm; this absorption resonance redshifts as $h$ decreases, and eventually becomes longer than 1000 nm (out of the measured spectral range) when $h$ reaches 50 nm. When $h$ is 75 nm, the resonance peak is at ~920 nm, close to the frequency of the pumping laser. Therefore, the pillar height dependence is attributed to the frequency matching between the plasmon resonance of D2PA and the pumping laser.

**Strong Enhancement Over a Large Area:** We characterized the enhancement factor of the UCL on the optimized D2PA substrate ($h = 75$ nm) by measuring the UCL spectra on both the D2PA substrate and the reference substrate under the exactly same experimental conditions, as shown in Figure 3a. The enhancement factor for each luminescence peak is determined by: $S_{up} \propto P_{n, pump}$

Where $S_{D2PA}$ and $S_{ref}$ is the UCL intensity, and $N_{D2PA}$ and $N_{ref}$ is the area density of the NaYF$_4$:Yb$^{3+}$/Er$^{3+}$-codoped nanocrystals, on the D2PA and the reference substrate, respectively. The $N_{D2PA}$ and $N_{ref}$ were obtained by carefully counting the particle numbers on high resolution SEM images. For $N_{D2PA} = 200$ particle/$\mu$m$^2$, and $N_{ref} = 900$ particle/$\mu$m$^2$, the enhancement factor was 310-fold and 100-fold for the peak at 660 nm and the peak at 550 nm, respectively. This value is 2 orders of magnitude larger than the previously reported results on the same type of nanocrystals.[1,30]

This large enhancement can be directly visualized with luminescence photography, as shown in Figure 3b–d. Both the D2PA

Figure 3. Enhanced upconversion luminescence on the optimized D2PA substrate. (a) Upconversion luminescence spectra on both the D2PA and reference substrates. Photoluminescence photography of NaYF$_4$:Yb$^{3+}$/Er$^{3+}$ nanocrystals at 550 nm (b), 660 nm (c) on the D2PA substrate, and on the reference substrate (d) measured at the same condition. The scale bar is 100 $\mu$m.
and reference samples were pumped by the same 0.04 W laser beam (980 nm) which was expanded into a 0.2 mm \times 0.2 mm area (100 W/cm²). Strong and uniform UCL emissions were recorded by a digital camera (DFK 31 BU03, ImagingSource) from the D2PA substrate at both 550 nm and 660 nm, but no UCL was observed from the reference substrate.

**Upconversion Luminescence vs. Pumping Power Density:** As a nonlinear effect, the pumping power density ($P_{\text{pump}}$) dependence of the upconversion luminescence ($S_{\text{up}}$) can be described by the power law: $S_{\text{up}} \propto P_{\text{pump}}^n$. However, unlike most of other nonlinear effects in which the exponent is constant, $n$ is pumping power dependent in upconversion luminescence. It is expected that the exponent $n$ is close to 2 at a low pumping power density; when $P_{\text{pump}}$ increases and the population of the first excited level becomes large, $n$ will decrease to 1; when $P_{\text{pump}}$ is extremely high, the population of the second excited level will becomes large and $S_{\text{up}}$ will saturate.\(^{[34]}\) As a result of the complicated power dependence of upconversion luminescence, the enhancement factor is a function of the pumping power density in most cases, except in the low pumping power regime where $n$ equals 2 same for all substrates.

In our experiments, we characterized the UCL signal $S_{\text{up}}$ at 660 nm as a function of $P_{\text{pump}}$ on both the D2PA and glass substrates. The result is plotted on a double-logarithmic scale in Figure 4. We found that $n$ (the slope of the log ($S_{\text{up}}$) - log ($P_{\text{pump}}$) curve) is approx. 1.8 (close to 2) on both substrates when $P_{\text{pump}} < 400$ W/cm². Thus, for the D2PA, the UCL enhancement factor is constant (∼310) when $P_{\text{pump}}$ is smaller than 400 W/cm².

**Lifetime Reduction of the Upconversion Luminescence:** The D2PA structure not only enhances the intensity of the local pumping light, but also increases the local density of states (LDOSs) which directly determines the lifetime of the excited states of the Er\(^{3+}\) ions.\(^{[35]}\) This can be reflected by the decay rate change of UCL in time-resolved measurements.

To measure the temporal behavior of UCL, we excited the samples with a series of square-shaped pulses which were generated by a beam chopper, Figure 1d. The temporal behaviors of UCL were measured on both D2PA and reference substrates, are shown in Figure 5. Unlike the normal down-conversion luminescence whose decay curve is a simple exponential function, the decay curve of UCL is much more complicated and cannot be expressed as a monoexponential function since it is not only related to the lifetime of the second excited level of Er\(^{3+}\), but also decided by the population of the first excited level of both Er\(^{3+}\), and Yb\(^{3+}\) ions, as well as the energy transfer rate between these ions. Thus, we determine the decay time $\tau$ by using the half maximum of the UCL intensity. We found that $\tau$ is ∼130 µs on the glass substrate, and ∼16 µs on the D2PA structure. It corresponds to an 8-fold enhancement in the decay rate, 4 times larger than the value observed on Au nanoparticles by Schietinger et al.\(^{[1]}\) We attribute this large decay rate...
enlargement to the fact that we are working on the resonance frequency of D2PA while nonresonant conditions were used in previous works.

**Origin of Large Upconversion Luminescence Enhancement:**
The observed large UCL enhancement comes from the strong resonant coupling between the Au nanodisks and the backplane of the D2PA. Due to its unique vertical design, D2PA is capable of packaging “hot” nanogaps (between the Au nanodisk, backplane and nanodots) together with a very high density (25 nanodisks per μm²), thus, creating a very large average enhancement for the local intensity of the excitation light. Unlike the conventionally used laterally aligned plasmonic structures (e.g. bowtie antennas), in which a high area density will induce strong couplings between neighboring components and make the resonance difficult to control, the resonance frequency of D2PA is mainly decided by the strong vertical coupling between nanodisks and backplane, enabling us to tailor the resonance frequency, and optimize the UCL enhancement by simply tuning the pillar height, as demonstrated in Figure 2.

To further understand the relation between the resonance frequency and the enhancement of the local pumping intensity, numerical simulations were performed. A 3-dimensional model was used based on the SEM measurements of D2PA. The electric field intensity was solved with a commercial finite-difference time-domain solver (Lumerical, Inc.), with periodic boundary conditions in the lateral directions, perfect match layers in the normal direction, a 1 nm mesh size, and a plane wave normal to the substrate as the excitation source. As shown in **Figure 6a**, smaller the pillar height is, longer the resonance wavelength is. This is consistent with the experimental results.

We also investigated the local electric field enhancement created by the D2PA substrates. As shown in Figure 6b, the electric fields are strongly localized and enhanced in the Au nanodisk-backplane gaps due to the strong vertical coupling between them as discussed in the introduction part. We plot the near-field light intensity (observed at the position marked in Figure 6b) as the function of wavelength (Figure 6c), and it clearly shows that the local electric field intensity reaches its maximum at the resonance frequency observed in the reflection spectra (Figure 6a). This explains the pillar height dependent UCL observed in the experiments.

In summary, we investigated the plasmon-enhanced upconversion luminescence of NaYF₄:Yb³⁺/Er³⁺ nanocrystals on a 3D plasmonic antenna architecture, the D2PA. We optimized the D2PA structure by tuning the pillar height h, and consequently the resonance frequency of the substrate, and found that, when h = 75 nm, the resonance frequency matches the pumping laser’s frequency and the enhancement factor of UCL reaches its maximum, 310-fold. This large enhancement is uniform (variation <10%) over a large area, and independent with the pumping power density P<sub>pump</sub> when P<sub>pump</sub> < 400 W/cm². We also measured the decay rate of UCL, and observed an 8-fold enhancement in decay rate, 4 times better than the result previously reported on single plasmonic particles.[1] These results not only deepen our understanding of the mechanism of the plasmon-enhanced UCL, but also provide a novel approach for making efficient thin-film UCL materials, which have a great potential in the fields of display, laser and solar energy.

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