Enhanced UV upconversion emission using plasmonic nanocavities

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Abstract: Upconversion of near infrared (NIR) into ultraviolet (UV) radiation could lead to a number of applications in bio-imaging, diagnostics and drug delivery. However, for bare nanoparticles, the conversion efficiency is extremely low. In this work, we experimentally demonstrate strongly enhanced upconversion emission from an ensemble of β -NaYF₄:Gd³⁺/Yb³⁺/Tm³⁺ @NaLuF₄ core-shell nanoparticles trapped in judiciously designed plasmonic nanocavities. In doing so, different metal platforms and nanostructures are systematically investigated. Our results indicate that using a cross-shape silver nanocavity, a record high enhancement of 170-fold can be obtained in the UV band centered at a wavelength of 345 nm. The observed upconversion efficiency improvement may be attributed to the increased absorption at NIR, the tailored photonic local density of states, and the light out-coupling characteristics of the cavity.

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References and links

1. F. Auzel, "Upconversion and anti-Stokes processes with f and d ions in solids," *Chem. Rev.* **104**(1), 139–174 (2004).
2. X. Li, F. Zhang, and D. Zhao, "Highly efficient lanthanide upconverting nanomaterials: progresses and challenges," *Nano Today* **8**(6), 643–676 (2013).
3. N. Bloembergen, "Solid state infrared quantum counters," *Phys. Rev. Lett.* **2**(3), 84–85 (1959).
4. M. R. Brown and W. A. Shand, "Infrared quantum counter action in rare earth doped fluoride lattices," *IEEE J. Quantum Electron.* **2**(8), 251–253 (1966).
5. A. Rapaport, J. Milliez, M. Bass, A. Cassanho, and H. Jenssen, "Review of the properties of up-conversion phosphors for new emissive displays," *J. Disp. Technol.* **2**(1), 68–78 (2006).
6. W. G. van Sark, J. de Wild, J. K. Rath, A. Meijerink, and R. E. Schropp, "Upconversion in solar cells," *Nanoscale Res. Lett.* **8**(1), 81 (2013).
7. S. Heer, O. Lehmann, M. Haase, and H.-U. Gudel, "Blue, green, and red upconversion emission from lanthanide-doped LuPO₄ and YbPO₄ nanocrystals in a transparent colloidal solution," *Angew. Chem. Int. Ed. Engl.* **42**(27), 3179–3182 (2003).
8. D. M. Wu, A. Garcia-Etxarri, A. Salleo, and J. A. Dionne, "Plasmon-enhanced upconversion," *J. Phys. Chem. Lett.* **5**(22), 4020–4031 (2014).
9. W. Park, D. Lu, and S. Ahn, "Plasmon enhancement of luminescence upconversion," *Chem. Soc. Rev.* **44**(10), 2940–2962 (2015).
10. F. Wang, D. Banerjee, Y. Liu, X. Chen, and X. Liu, "Upconversion nanoparticles in biological labeling, imaging, and therapy," *Analyst (Lond.)* **135**(8), 1839–1854 (2010).
11. C. Wang, L. Cheng, and Z. Liu, "Drug delivery with upconversion nanoparticles for multi-functional targeted cancer cell imaging and therapy," *Biomaterials* **32**(4), 1110–1120 (2011).

12. M. L. Viger, M. Grossman, N. Fomina, and A. Almutairi, "Low power upconverted near-IR light for efficient polymeric nanoparticle degradation and cargo release," *Adv. Mater.* **25**(27), 3733–3738 (2013).
13. G. S. Yi and G. M. Chow, "Water-soluble NaYF₄:Yb,Er(Tm)/NaYF₄/polymer core/shell/shell nanoparticles with significant enhancement of upconversion fluorescence," *Chem. Mater.* **19**(3), 341–343 (2007).
14. L. Pan, M. He, J. Ma, W. Tang, G. Gao, R. He, H. Su, and D. Cui, "Phase and size controllable synthesis of NaYbF₄ nanocrystals in oleic acid/ionic liquid two-phase system for targeted fluorescent imaging of gastric cancer," *Theranostics* **3**(3), 210–222 (2013).
15. J. Zhao, S. Ji, and H. Guo, "Triplet-triplet annihilation based upconversion: from triplet sensitizers and triplet acceptors to upconversion quantum yields," *RSC Advances* **1**(6), 937–950 (2011).
16. C. M. Johnson, P. J. Reece, and G. J. Conibeer, "Slow-light-enhanced upconversion for photovoltaic applications in one-dimensional photonic crystals," *Opt. Lett.* **36**(20), 3990–3992 (2011).
17. Y. Yang, P. Zhou, W. Xu, S. Xu, Y. Jiang, X. Chen, and H. Song, "NaYF₄:Yb³⁺,Tm³⁺ inverse opal photonic crystals and NaYF₄:Yb³⁺,Tm³⁺/TiO₂ composites: synthesis, highly improved upconversion properties and NIR photoelectric response," *J. Mater. Chem. C Mater. Opt. Electron. Devices* **4**(4), 659–662 (2016).
18. B. Herter, S. Wolf, S. Fischer, J. Gutmann, B. Blasi, and J. C. Goldschmidt, "Increased upconversion quantum yield in photonic structures due to local field enhancement and modification of the local density of states—a simulation-based analysis," *Opt. Express* **21**(S5 Suppl 5), A883–A900 (2013).
19. A. C. Pan, C. Del Canizo, E. Canovas, N. M. Santos, J. P. Leitao, and A. Luque, "Enhancement of up-conversion efficiency by combining rare earth-doped phosphors with PbS quantum dots," *Sol. Energy Mater. Sol. Cells* **94**(11), 1923–1926 (2010).
20. W. Zou, C. Visser, J. A. Maduro, M. S. Pshenichnikov, and J. C. Hummelen, "Broadband dye-sensitized upconversion of near-infrared light," *Nat. Photonics* **6**(8), 560–564 (2012).
21. S. Schietinger, T. Aichele, H. Q. Wang, T. Nann, and O. Benson, "Plasmon-enhanced upconversion in single NaYF₄:Yb³⁺/Er³⁺ codoped nanocrystals," *Nano Lett.* **10**(1), 134–138 (2010).
22. N. Liu, W. Qin, G. Qin, T. Jiang, and D. Zhao, "Highly plasmon-enhanced upconversion emissions from Au@β-NaYF₄:Yb,Tm hybrid nanostructures," *Chem. Commun. (Camb.)* **47**(27), 7671–7673 (2011).
23. M. Saboktakin, X. Ye, S. J. Oh, S. H. Hong, A. T. Fafarman, U. K. Chettiar, N. Engheta, C. B. Murray, and C. R. Kagan, "Metal-enhanced upconversion luminescence tunable through metal nanoparticle-nanophosphor separation," *ACS Nano* **6**(10), 8758–8766 (2012).
24. W. Zhang, F. Ding, and S. Y. Chou, "Large enhancement of upconversion luminescence of NaYF₄:Yb³⁺/Er³⁺ nanocrystal by 3D plasmonic nano-antennas," *Adv. Mater.* **24**, 236–241 (2012).
25. M. Saboktakin, X. Ye, U. K. Chettiar, N. Engheta, C. B. Murray, and C. R. Kagan, "Plasmonic enhancement of nanophosphor upconversion luminescence in Au nanohole arrays," *ACS Nano* **7**(8), 7186–7192 (2013).
26. K. T. Lee, J. H. Park, S. J. Kwon, H. K. Kwon, K. W. Kwak, H. S. Jang, S. Y. Kim, J. S. Han, S. H. Lee, D. H. Shin, H. Ko, I. K. Han, B. K. Ju, S. H. Kwon, and D. H. Ko, "Simultaneous enhancement of upconversion and downshifting luminescence via plasmonic structure," *Nano Lett.* **15**(4), 2491–2497 (2015).
27. W. H. de Jong and P. J. A. Borm, "Drug delivery and nanoparticles: applications and hazards," *Int. J. Nanomedicine* **3**(2), 133–149 (2008).
28. C. Lantigua, S. He, M. A. Bouzan, W. Hayenga, N. J. Johnson, A. Almutairi, and M. Khajavikhan, "Engineering upconversion emission spectra using plasmonic nanocavities," *Opt. Lett.* **39**(13), 3710–3713 (2014).
29. S. E. Ivanova, A. M. Tkachuk, A. Mirzaeva, and F. Pellé, "Spectroscopic study of thulium-activated double sodium yttrium fluoride Na_{0.4}Y_{0.6}F_{2.2}:Tm³⁺ crystals. I. Intensity of spectra and luminescence kinetics," *Opt. Spectrosc.* **105**(2), 228–241 (2008).
30. J. F. Suyver, A. Aebischer, D. Biner, P. Gerner, J. Grimm, S. Heer, K. W. Krämer, C. Reinhard, and H. U. Güdel, "Novel materials doped with trivalent lanthanides and transition metal ions showing near-infrared to visible photon upconversion," *Opt. Mater.* **27**(6), 1111–1130 (2005).
31. N. J. J. Johnson and F. C. J. M. van Veggel, "Lanthanide-based heteroepitaxial core-shell nanostructures: compressive versus tensile strain asymmetry," *ACS Nano* **8**(10), 10517–10527 (2014).
32. N. J. J. Johnson, A. Korinek, C. Dong, and F. C. J. M. van Veggel, "Self-focusing by Ostwald ripening: a strategy for layer-by-layer epitaxial growth on upconverting nanocrystals," *J. Am. Chem. Soc.* **134**(27), 11068–11071 (2012).
33. K. Zheng, W. Qin, C. Cao, D. Zhao, and L. Wang, "NIR to VUV: Seven-Photon Upconversion Emissions from Gd³⁺ Ions in Fluoride Nanocrystals," *J. Phys. Chem. Lett.* **6**(3), 556–560 (2015).
34. H.-X. Mai, Y.-W. Zhang, R. Si, Z. G. Yan, L. D. Sun, L. P. You, and C. H. Yan, "High-quality sodium rare-earth fluoride nanocrystals: controlled synthesis and optical properties," *J. Am. Chem. Soc.* **128**(19), 6426–6436 (2006).
35. Z. Li and Y. Zhang, "An efficient and user-friendly method for the synthesis of hexagonal-phase NaYF₄:Yb,Er/Tm nanocrystals with controllable shape and upconversion fluorescence," *Nanotechnology* **19**(34), 345606 (2008).
36. E. M. Purcell, "Spontaneous emission probabilities at radio frequencies," *Phys. Rev.* **69**, 681 (1946).
37. M. Khajavikhan, A. Simic, M. Katz, J. H. Lee, B. Slutsky, A. Mizrahi, V. Lomakin, and Y. Fainman, "Thresholdless nanoscale coaxial lasers," *Nature* **482**(7384), 204–207 (2012).
38. G. M. Akselrod, C. Argyropoulos, T. B. Hoang, C. Ciraci, C. Fang, J. Huang, D. R. Smith, and M. H. Mikkelsen, "Probing the mechanisms of large Purcell enhancement in plasmonic nanoantennas," *Nat. Photonics* **8**(11), 835–840 (2014).

1. Introduction

Photon upconversion (UC) has been the focus of considerable attention in recent years [1,2]. Upconversion represents an anti-Stokes process, which involves the sequential absorption of two or more photons in the infrared (IR) or near infrared (NIR) spectral range, leading to luminescence at a shorter wavelength, typically in the visible (Vis) or ultraviolet (UV) [3]. In inorganic systems, UC is based on the availability of multiple long-lived, metastable excited states, typically encountered in rare-earth elements. Thus far, photon UC has been utilized in various applications such as IR quantum counters, solid-state lasers, in lighting, displays, and solar cells [4–6]. In recent years, the successful synthesis of colloiddally stable solutions of monodisperse upconverting nanoparticles (UCNPs) with diameters on the order and less than 50 nm has opened up new opportunities in this general area [7–9]. It is envisioned that such UCNPs may replace dye molecules as diagnostic and therapeutic tools for biological imaging, or can be used in targeted drug delivery [10–12]. Unfortunately, the conversion efficiency of UCNPs can be even lower than their bulk counterparts, something that imposes a serious challenge in utilizing these nanoparticles in most settings. Substantial effort has been dedicated in improving the UCNPs' upconversion efficiency by studying their surface chemistry, designing new host media in crystalline and/or amorphous phases, and by introducing a variety of assisting dopants to facilitate nonlinear energy transfers [13–15]. Clearly, for a given UCNP, the efficiency is predetermined by the chemistry and synthesis methods used, which governs the electronic density of states and quenching effects. Yet, as indicated in a number of studies, it is possible to further boost the UCNPs' luminescence by appropriately engineering the electromagnetic environment they are embedded in. This can be accomplished for example using photonic crystals, mixing UCNPs with quantum dots, and accompanying UCNPs with dye antennas [16–20]. Plasmonics provides yet another promising route towards this goal. Plasmonic assisted upconversion has been the focus of a number of studies in the past few years [21–26]. Most of these investigations consider scenarios in which either individual nanoparticles are covered with a metallic coating or metal nanoparticles are introduced in the vicinity of a UCNP. However, in some applications, particularly those aiming towards targeted drug delivery, such extreme reductions in size down to a single nanoparticle may not be advantageous [27]. At this point, the question naturally arises as to whether more versatile and relatively larger plasmonic configurations such as metallic nanocavities can be used to improve the conversion efficiencies.

In this work, using silver cross-shape plasmonic nanocavity, we demonstrate a record high improvement (a 170-fold increase) in the generation of UV radiation centered at a wavelength of 345 nm. In this configuration, approximately ten β -NaYF₄: Gd³⁺/Yb³⁺/Tm³⁺ @NaLuF₄ core-shell nanoparticles with diameters on the order of 30 nm (core particles are only 17–18 nm) are first embedded in PMMA and then encapsulated in a silver cavity. The increased upconversion is attributed to the presence of the metallic resonator that provides higher absorption at NIR, larger electromagnetic local density of states, and more efficient light outcoupling [28]. Furthermore, we systematically investigate the UV and visible upconversion enhancement in a number of nanoresonators as well as in several metal platforms including silver (Ag), aluminum (Al), and gold (Au). Such larger nanocavities may provide an effective carrier for drug molecules in targeted drug delivery applications.

2. Synthesis and upconversion processes in NaYF₄: Yb³⁺, Tm³⁺ material system

Fig. 1. (a) Energy diagram for the upconversion nanoparticles NaYF₄:Yb³⁺/Tm³⁺. Solid arrows indicate absorption lines and radiative transitions; dashed arrows represent nonlinear energy transfers. (b) The primary radiative transitions and their corresponding nominal probabilities. (c) A solution of NaYF₄:20%Yb³⁺/0.5%Tm³⁺ nanoparticles illuminated by a 980 nm laser. (d) A transmission electron micrograph (TEM) of the β-phase UCNPs.

The pertinent energy bands of NaYF₄: Yb³⁺, Tm³⁺ upconverting material are depicted in Fig. 1(a). In this solid state system, NaYF₄ is the host crystal, and Ytterbium ions as sensitizers are the primary absorption centers at 980 nm. The energy absorbed by the sensitizer ions is transferred nonlinearly to the activators – in this case the Thulium ions. This energy transfer is governed by the proximity of the respective ions in the crystal lattice, and is by nature orders of magnitude faster than the decay rates associated with the ions' energy levels. Such longlifetimes (in the millisecond-regime) allow the electrons to climb the energy ladder in the activator by absorbing more than one photon at 980 nm. The dominant electronic transitions and their nominal probabilities are tabulated in Fig. 1(b). For the above upconverting material,

the conversion efficiencies to the Vis/UV bands are on the order of 1.0/0.04 percent of the total luminescence [29,30]. Clearly, such low conversion efficiencies impose a challenge in utilizing UCNPs in a host of envisioned applications.

In recent years, there has been considerable research interest towards increasing the conversion efficiency of UCNPs by optimizing their synthesis conditions. These efforts include surface engineering and passivation, fine-tuning of the size of nanoparticles, introducing assisting dopants, and exploring new crystalline phases for nanoparticles like cubic and hexagonal states [13–15]. By modifying the synthesis procedure, our group has recently demonstrated β-NaYF₄: 10%Gd/20%Yb³⁺/0.5%Tm³⁺@ NaLuF₄ nanoparticles with enhanced emission in the UV-bands [31].

The core-shell nanoparticles of NaYF₄: Gd/Yb/Tm@NaLuF₄ used in this study were prepared using an epitaxial layer-by-layer growth method on upconverting NaYF₄ nanocrystal [31–33]. Gd³⁺ doping of nanoparticles is known to facilitate the formation of a hexagonal phase. First, the cubic phase NaLuF₄ nanoparticles were synthesized by thermal decomposition of 2 mmol NaCF₃COO and 2 mmol Lu (CF₃COO)₃ in a mixture of 1-octadecene, oleic acid and oleylamine [34]. The resulting NaLuF₄ nanoparticles were then washed and dispersed in hexane. Core particles were synthesized based on diffusion-limited growth of the nanocrystals [35]. In typical synthesis, 0.695 mmol Yttrium acetate, 0.2 mmol ytterbium acetate, 0.1 mmol gadolinium acetate, and 0.005 mmol thulium acetate were dissolved in 15 mL 1-octadecene, and 6 mL oleic acid. This mixture was heated to 120°C for 45 min and then cooled down to room temperature. Once cooled, 10 mL methanol solution

containing 4 mmol NH_4F and 2.5 mmol NaOH were added. The system was slowly heated until all methanol was removed and kept at 300°C for 60 minutes to form the core nanoparticles. Cubic phase NaLuF_4 nanoparticles were then injected to provide the shell. After another 60 minutes, the mixture was cooled down to room temperature, precipitated and washed by ethanol. The final products were dispersed in 5 mL chloroform. Figure 1(c) shows a solution of the above upconverting nanoparticles in chloroform. The blue-violet hue indicates an enhanced UV emission. The brightness of the hexagonal β -phase NaYF_4 is up to two orders of magnitude greater than the cubic α - NaYF_4 . A transmission electron micrograph (TEM) image of nanoparticles showing the β -stable phase with hexagonal cross section is displayed in Fig. 1(d).

3. Upconversion enhancement through plasmonics nanocavities

Beyond synthesis, the emission spectrum of an upconverting nanoparticle can be further tuned by changing its photonic environment. So far, decorating individual UCNPs by gold nanoparticles has been perhaps one of the most promising approaches [21–23]. In this arrangement, the localization of the field due to the presence of metallic nanoparticles tends to enhance the radiative decay rates through the Purcell effect [36]. It should be noted that while any further miniaturization of nanoparticles can in principle result in yet higher radiative rates, the proximity to metal nanoparticles introduces non-radiative transitions and dissipative losses. The interplay between these two effects sets an upper limit on the maximum achievable efficiency improvement from a single particle. In a recent study, a 30 to 50-fold upconversion enhancement in the visible range was reported when a UCNP was covered with a 5-10 nm dielectric spacing layer before it was coated by metallic nanoparticles [22].

In order to overcome the limitations imposed by the non-radiative decay rates, one can use an ensemble of upconverting nanoparticles in a more structured arrangement such as those encountered in nanocavities [28]. There are several advantages associated with this approach: (i) it reduces the non-radiative transitions and dissipative losses per UCNP, (ii) the resonator allows to engineer the spectral distribution of the photonic density of states, (iii) the cavity provides a more effective interface for transferring energy to the targets in the mesoscopic range. This approach is particularly advantageous in drug delivery applications for which it has been suggested that relatively large (diameter >100 nm) nanoparticles may be needed for loading a sufficient amount of drug cargo [27]. In what follows we numerically and experimentally investigate these aspects for a class of nanocavities based on cross-shape geometries.

Introducing a cavity in the vicinity of an atomic system can localize the field and alter the material's absorption and emission characteristics. Since UC is a nonlinear process, increasing the NIR absorption (effectively increasing the incident power delivered to nanoparticles) can have a drastic effect in improving the conversion efficiency at various spectral bands. The ground state absorption (GSA) of the sensitizer ions, as well as the excited state absorption (ESA), and stimulated emission (STE) processes in the activator scale up with the incoming photon flux density. These in turn influence the overall dynamics of the UC system. A rate equation model incorporating these aspects was previously reported by our group [28].

To evaluate the absorption enhancement at the 980 nm NIR excitation wavelength, we utilize finite element -fold increase in absorption when compared to an unpatterned film of the same area. The proposed plasmonic nanocavities also alter the photonic local density of states (LDOS) at the resonant transition frequencies of the sensitizer and activator. The transition probability P_{if} of a spontaneous emission process at a frequency ω_f is governed by Fermi's golden rule, $P_{if} = (2\pi / \hbar) |M_{if}|^2 \rho(\mathbf{r}, \omega_f)$, where M_{if} represents the dipole

transition matrix element, and $\rho(\mathbf{r}, \omega_f)$ is the local density of states [35]. Since the output luminescence at frequency ω_f is linearly proportional to the transition rate of methods (FEM) (Figs. 2(a) and (b)). In this simulation performed by COMSOL Multiphysics software, we assume that the polymer containing UCNPs is encapsulated in a metallic nanocavity (Fig. 2(b)). For simulation purposes, the net absorption coefficient of such UCNP enriched polymer is taken to be 5 cm^{-1} [28]. Figures 2(a) and (b) show the result of such simulations performed for a nanocavity with a cross-shape geometry surrounded by air and silver walls (50 nm), respectively. The structure is illuminated by a linearly polarized plane wave directed towards its opening aperture (in this case from the top). For metallic cross-shape cavity, the FEM simulation predicts a 16th corresponding energy level, one might be able to fine tune the upconversion rate at the spectral band of interest [37,38]. Figure 2(c) shows the spectrum of the LDOS for a cross-shape silver cavity. Once the absorption enhancement and LDOS at various transitions are calculated, one can incorporate this data in the rate equation model to find the resulting modified spectra of the UCNPs trapped in plasmonic nanocavities [28].

Finally, a nanocavity operates both as an energy storage unit and as an antenna. While at some wavelengths, the energy generated in the cavity is fully trapped, at certain other bands, the resonator effectively outcouples the radiation. For the cross-shape cavity of Fig. 2(b), a FEM simulation is performed by assuming radiating dipoles at random locations across the resonator. The average spectrum of the emitted power normalized to that of a plain film is depicted in Fig. 2(d). Similar simulations are performed for other nanocavity systems.

Fig. 2. Electromagnetic response of a cross-shape nanocavity. (a) A cross-shape cavity when surrounded by air and the associated absorption profile. (b) Same as in (a). Here the resonator is surrounded by silver walls. For visual purposes, the absorption profiles in (a) and (b) are normalized differently. (c) The local density of states. The four curves represent different simulations, each carried with 10 random dipoles. (d) The ratio of outcoupling from dipoles randomly dispersed in the cavity to that when these same dipoles are embedded in a UCNP plain film.

4. Fabrication procedure and measurement station

In order to experimentally characterize upconversion enhancement in the presence of plasmonic resonators, several nanocavities containing UCNPs embedded in PMMA are implemented. The steps involved in the fabrication process are shown in Fig. 3(a)-(g). First, after cleaning the surface of a microscope glass slide, a 200 nm thick metal film (Aluminum, gold, or silver) is deposited by e-beam evaporation at an average rate of 0.1 Å/s and is covered by a 300 nm spin-coated positive e-beam resist (polymethyl methacrylate (PMMA) 950 A4). The geometrical patterns of the nano-cavities are transferred to the PMMA using e-

beam lithography (prebake: 180 °C for 90 s, lithography: Leica e-beam system operating at 50 KV, develop: 1:3 MIBK to IPA). A 200 nm thick metal film is then deposited using e-beam evaporation to define the walls of the nano-cavities. Next, the remaining bare PMMA is removed along with the metallic film deposited on its top surface; leaving behind empty metallic cavities that are subsequently filled by UCNP enriched PMMA using a spin-coating process (200 nm thickness). The final product consists of metallic nano-cavities with randomly dispersed nanoparticles in and around them. Using the above procedure, nanoresonators of various geometries (rings, crosses, concentric rings and squares) are realized. In addition to the samples containing nanocavities, two types of control samples are fabricated: (i) glass substrate covered by UCNP enriched PMMA thin film, (ii) glass substrate with a 200 nm thick metallic film covered by the UCNP-PMMA thin film. The measurements performed on these samples are used for comparison purposes. Figure 3(h) shows an SEM image of a final pattern- the white dots in the cavity are UCNPs. The fabrication procedure was found not to cause aggregation of nanoparticles inside the cavity – an undesired effect that can lead to excess non-radiative transitions and quenching.

Fig. 3. Nanofabrication procedure. (a)-(g) The steps involved in the fabrication of the nanocavities with UCNPs. (h) A scanning electron microscope image of a ring-shape cavity.

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Fig. 4. (a) A schematic of upconversion nanoparticle. The dimensions of the four nanocavity structures studied in this paper. (b) cross shape, (c) square, (d) ring, and (e) concentric rings nanocavities.

Fig. 5. A schematic of the lock-in detection characterization set-up, with a built-in confocal microscope for adjusting the pump with respect to the patterns.

In order to increase measurement accuracy by reducing the effect of fabrication imperfections, we obtain the average performance of an array of identical nanocavities extending over an area of approximately $100 \times 100 \mu\text{m}^2$. A schematic picture of the nanoparticle along with the geometric shape and dimensions of the patterns used in this study are depicted in Fig. 4(a)-(e). All patterns have a thickness of 200 nm and are sandwiched between air and metal from top and bottom, respectively. The samples are then optically excited by a 980 nm continuous-wave laser beam focused on an area of $\sim 80 \mu\text{m}^2$. Even though several unit cells are illuminated by the beam, the upconverted emission from adjacent cavities is generally incoherent – hence no interference effect is expected. All experiments reported in this manuscript are performed at a fixed pump power of $\sim 150 \text{ mW}$. The luminescence from the UCNPs in the visible and UV is then directed to a spectrometer followed by a lock-in detection scheme (lock-in amplifier and GaP detector) in order to collect the spectrally resolved upconversion emission. The set-up is equipped with a built-in confocal microscope (through the white light source and the kinematic mirror) to adjust the location of the pump beam with respect to the patterns. A schematic of this characterization set-up is shown in Fig. 5.

5. Experimental results

In this study, we focus our attention on the conversion efficiency from NIR to four spectral bands in the lower visible and UVA frequencies, corresponding to peaks appearing at approximately 475, 450, 360, 345 nm. The fabricated samples can be divided into three categories: (i) those containing arrays of nanocavities, (ii) a thin-film of UCNP-PMMA on glass, (iii) those with a thin-film of UCNP-PMMA on a metal layer. A collective study is carried out to compare various cavity designs as well as different metal platforms. Figures 6(a)-(c) display the measured emission spectra collected from a variety of nanocavity arrays, from UCNP-films on glass, as well as UCNP-films on metal layers. The reported emission spectra are all based on the same unit of intensity and as a result comparing the performance of different structures and platforms is justified.

To begin with, the UCNP-PMMA films deposited on all three metals (Ag, Al, Au) show an enhanced emission in all the spectral bands when compared to the films directly spun on a glass substrate. This could be attributed to multiple reflections taking place within the film (sandwiched between the metal and air), thus increasing the absorption at NIR and directing more upconversion emission back to the spectrometer. This can be confirmed considering that samples with Ag and Al coatings (reflections at 350 nm: 0.71 and 0.92 respectively) show more enhancement than gold coated samples (Au reflection at 350 nm: 0.34). In the visible domain, silver is expected to be as good as aluminum (reflection at 450 nm: ~ 0.91), while the reflection from gold remains low.

Furthermore, all samples involving nanocavity arrays outperform those in which UCNP-PMMA is directly spun on a metallic film. These measurements suggest that the observed improvement is a direct outcome of the presence of nanocavities, which in turn can lead to enhanced absorption as well as of modified local density of states and outcoupling signature. In general, the rate of upconversion enhancement varies across the spectral bands- suggesting that nanocavities can be employed to generate customized spectral features. The absorption enhancement is expected to have a more pronounced effect at shorter wavelengths, while the photonic density of states and outcoupling ratio tend to display distinct spectral signatures depending on the cavity geometry/metal constituent. Generally, it is clear from Fig. 6 that in all cases, silver cavities demonstrate higher upconversion efficiencies in the spectral bands of interest as compared to their gold and aluminum counterparts.

Fig. 6. Measurement results. Upconversion spectra for a number of patterns and nanocavities using (a) silver, (b) gold, (c) aluminum. All three diagrams are normalized to the same arbitrary units of intensity.

The direct measurement results presented in Fig. 6 can only be used to compare the performance of arrays of nanocavities. In order to determine the enhancement factor associated with a single nanocavity, one must take into account the geometric ratio between

the area occupied by the plasmonic nanocavity with respect to the total area of a unit cell in each array system. Figure 7(a)-7(c) shows the calculated upconversion spectra for single nanocavities of various geometries on different metal systems. Again, it should be noted that since the emission from array elements is not coherent, no interference effect or far-field pattern is expected. The lack of coherence between individual cavities is mainly due to the relatively long lifetime of all transitions involved ($\sim$ millisecond) in comparison to the coupling strengths between array elements ($<$ nanosecond). Once the fill-factor is considered, the cross-shape silver cavity appears to be the one with the largest upconversion efficiency enhancement of 170-fold at the spectral band around 345 nm. This is the highest conversion efficiency ever reported at UV frequencies. Interestingly, this cavity is both the smallest in size and has the sharpest edges. Figure 7(d) summarizes the enhancements associated to a variety of plasmonic nanocavities when compared to the unpatterned UCNPs films on glass. The result of this study is in agreement with the rate equation model presented in [28].

Fig. 7. Single cavity upconversion enhancement (a-c). (d) Comparison of the upconversion enhancement between different cavity designs and metal platforms at four spectral bands in the visible and near ultraviolet frequencies. The enhancement is calculated as the ratio of the emitted light from a single nanocavity to that emanating from the same area of UCNPs films on glass.

5. Discussion and future work

In this work we have shown that encapsulating an ensemble of UCNPs in a metallic nanocavity provides a new route towards more efficient UCNPs systems in terms of overall yield in the visible and near infrared regime. The improved upconversion rates can be attributed to the increased absorption at near infrared, the higher density of photonic states and, the effective emitting properties of metal cavities. To further investigate the role of different mechanisms in enhancing upconversion emission the time decay from different energy bands can be measured directly. It should be noted that in upconverting ions with many transition levels, the time decay measurements cannot uniquely identify what causes the

change in the decay rates, whether it is absorption, density of states, or even nonlinear cross relaxation and energy transfers. In future works, similar nanocavities containing UCNPs dispersed in biodegradable polymers will be designed and tested. After loading the drug cargo, such nanocavities could be used as a vehicle in targeted drug delivery applications.

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