Enhancement of Near-Infrared-to-Visible Upconversion Luminescence Using Engineered Plasmonic Gold Surfaces

Hari P. Paudel,[†] Lanlan Zhong,[‡] Khadijeh Bayat,[†] Mahdi Farrokh Baroughi,[†] Steve Smith,[‡] Cuikun Lin,[§] Chaoyang Jiang,[§] Mary T. Berry,[§] and P. Stanley May^{*,§}

⁺Department of Electrical Engineering and Computer Science, South Dakota State University, Brookings, South Dakota 57007, United States

^{*}Nanoscience and Nanoengineering Department, South Dakota School of Mines & Technology, Rapid City, South Dakota 57701, United States

[§]Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069, United States

S Supporting Information

ABSTRACT: An engineered plasmonic gold surface, specifically designed to couple with 980 nm radiation, is shown to enhance near-infrared-to-visible upconversion luminescence from a monolayer of β -NaYF₄: 17%Yb, 3%Er nanocrystals in poly(methyl methacrylate) on that gold surface. Confocal imaging of upconversion luminescence from the surface is used to characterize the nature of the enhancement. It is shown that the luminescence data were acquired below the so-called "high power limit" for excitation, but some saturation was evident, as the observed power dependence was less than quadratic. Over the range of excitation power densities used, the intrinsic enhancement factor for upconversion from the pat-



terned surface was greater than a factor of 3 but decreased slowly with increasing excitation power. The red and green upconversion were enhanced by similar factors, which would support the intensification of the excitation field by the plasmonic surface as being the mechanism of enhancement. In the absence of other enhancement or quenching mechanisms, the data imply an approximate 2-fold magnification of the excitation field intensity relative to smooth gold.

INTRODUCTION

Short-wavelength light can be produced from long-wavelength sources by a variety of optical processes, including second-harmonic generation (SHG), simultaneous two-photon absorption (TPA), and upconversion (UC). The upconversion process is unique in this group in that it involves *sequential* absorption or energy-transfer events, all of which involve nonvirtual, long-lived electronic states of a suitable phosphor.¹ UC, therefore, has the potential to be much more efficient compared to SHG and TPA and does not require a coherent excitation source.^{2,3}

Although the lineage of modern, solid-state UC materials dates back to the 1960s, there has been a recent explosion of interest in upconverters for device and sensing applications.^{4–7} The origins of this renewed interest can probably be traced to the introduction of efficient, solvent-dispersible nanocrystalline UC materials (NaYF₄) activated by trivalent lanthanide ions (Ln³⁺).⁸ UC nanocrystals have applications in biological sensing,^{5,7} photodynamic therapy,^{5,9,10} spectral conversion in solar cells,⁶ 3D optical displays,^{11–14} and security printing.¹⁵ The use of upconverters in a nanocrystalline form dramatically increases their processability, in terms of incorporation into composite materials, and provides high spatial resolution and biocompatibility for

sensing applications. There is particular interest in upconversion phosphors that can efficiently convert near-infrared (NIR) excitation from inexpensive diode lasers into visible luminescence.² NIR-to-visible and NIR-to-NIR upconverters have great potential in areas such as nanolabels for bioimaging,^{4,5,16-18} because the use of NIR excitation virtually eliminates unwanted fluorescence background signal. NIR-to-visible UC nanocrystals have been proposed for photodynamic therapy applications,^{5,9,10} for which the use of NIR excitation is very advantageous due to its high penetration depth in biological tissue. By far the most wellstudied NIR-to-visible UC nanocrystals to date are based on the Ln^{3+} -doped β -NaYF₄ lattice, wherein Yb³⁺ is used as a sensitizer, absorbing 980 nm light, and either Er^{3+} or Tm^{3+} is used as the visible activator. They are the most efficient upconverters known, and a variety of synthetic methods have been described for producing solvent-dispersible nanoparticles with controlled size, shape, and capping ligand.^{2,8,14,18–31}

In the limit of high excitation flux, the intrinsic quantum efficiencies of UC phosphors can be quite high. Suyver et al. estimate

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that, in the high-power excitation regime, ~50% of the NIR photons absorbed by β -NaYF₄: 2%Er³⁺, 18% Yb³⁺ contribute directly to mechanisms leading to the emission of visible light.³² However, in the low-excitation-power region, UC has a quadratic (or even higher-order) dependence on excitation, so that luminescence intensity drops precipitously with excitation power. A primary obstacle to the incorporation of UC phosphors into real devices and applications has been the inability to obtain high upconversion efficiencies under modest excitation flux.

It is well-known that engineered and colloidal noble-metal surfaces can be used to influence the optical properties (e.g., quantum efficiency, absorbance, polarization, directional emission, excited-state lifetime) of a wide variety of luminescent materials.³³⁻³⁹ Luminescence efficiencies of both organic and inorganic phosphors can be enhanced by their suitable proximity to a metal surface. The enhancement mechanisms of interest here are those involving the interaction of the plasmons supported by the metal surface with the phosphor, resulting in a modification of the local electromagnetic environment of the phosphor. Two fundamental types of processes contribute to luminescence enhancement: amplification of the electric-field of excitation light in the vicinity of the metal surface and modification of the intrinsic radiative transition rates of the phosphor.33,34,38 The first effect is the better understood and works by increasing the effective excitation rate of the phosphor through amplification of the local electromagnetic field at the phosphor position. It is this effect that is mainly responsible for surface-enhanced Raman scattering (SERS).³³ The second effect works through modification of the intrinsic radiative (and nonradiative) processes of the phosphor via near-field interaction with the metal surface. This effect can either enhance or quench luminescence, depending on whether the interaction facilitates radiation to the far field (i.e., emission of photons) or results in a net loss of phosphor excitation to the metal surface.³⁶

Recent progress has been reported in achieving enhancement of UC emission using noble-metal nanoparticles $^{40-50}$ or metallic subwavelength aperture arrays.⁵¹ The majority of these studies are on glasses doped with Er^{3+,41} Er³⁺-Yb^{3+,46,47} or Pr^{3+} (refs 42, 44) and embedded with Ag nanoparticles. In a similar system, a Er³⁺-Yb³⁺ codoped tellurite thin film was deposited on glass substrates containing metal nanoparticles near the surface by way of an electric-field assisted ion diffusion process.⁴⁹ Feng et al. reported the enhancement of red and green UC from dense monolayers of β -NaYF₄:Er,Yb nanocrystals by Ag nanowires,⁴⁵ and Zhang, et al. claimed a 5-fold increase in UC from β -NaYF₄:Er,Yb nanocrystals in proximity to gold island films.⁵⁰ Spatial information regarding the interaction of plasmonic structures with UC phosphors has been obtained by using a Ag waveguide to achieve controlled focus of surface plasmon polaritons in the vicinity of the phosphor⁴³ and by combining confocal and atomic force microscopy to study the interaction of individual NaYF₄:Er,Yb nanocrystals with gold nanospheres.⁴⁸ In an interesting twist, Verhagen et al. used 1480 nm-to-980 nm UC from Er³⁺ to investigate the field enhancement of incident NIR light on subwavelength aperture arrays in a thin Au film.⁵¹

In the present study, we use confocal microscopy to characterize the enhancement of NIR-to-visible UC from a thin film of β -NaYF₄: 3% Er, 17% Yb nanocrystals (65 nm) in poly(methyl methacrylate) (PMMA). The UC film is spin coated onto an engineered plasmonic surface, consisting of gold nanopillars on a continuous gold film, which is specifically designed to couple with the NIR excitation wavelength.⁵² The UC enhancement is characterized relative to emission from the UC film on the smooth gold surface, adjacent to the plasmonic pattern. The results of this study demonstrate that it is feasible to use engineered plasmonic surfaces of intentional design to enhance NIR-to-visible upconversion luminescence from nanocrystalline systems. Such a strategy offers distinct advantages over the use of colloidal films of metal nanostructures, for which the nature and spatial distribution of plasmonic "hot spots" are difficult to control.

EXPERIMENTAL METHODS

Fabrication of Patterned Gold Surfaces. Electron beam lithography, followed by a lift-off process, was used to fabricate the patterned gold surfaces. A glass or silicon substrate was first cleaned using a RCA-I cleaning procedure. A 10 nm chromium layer was deposited on the cleaned substrate (for adhesion of gold) and a 100 nm thick gold layer was then deposited over the chromium. Both metals were deposited using rf sputtering from a Torr combination system. The gold surface was then spincoated with a 300 nm thick layer of electron beam resist (495 PMMA polymer; 6% solid in Anisole). The spin coating was done at 4000 rpm for 45 s and then prebaked for 1 min at 180 °C on a hot plate. A Hitachi scanning electron microscope, S-3400N, with an NPGS nanopatterning accessory was used to pattern the design in a 100 μ m \times 100 μ m square. The photoresist was patterned with an electron-beam dose of 350 μ C/cm². The exposed sample was developed in methyl isobutyl ketone (MIBK)/isopropanol (IPA):1/3 solution, purchased from Microchem, for 25 s. A 70 nm gold layer was deposited above the patterned surface by e-beam evaporation using a CHA e-Beam evaporator. Directional deposition was necessary, both for the formation of sharp nanopillars and for a successful lift-off process. Finally, the sample was immersed in a Remover PG solution at room temperature for 4 h to lift-off the PMMA layer. The height of the nanopillars was measured using a KLA TENCOR P-16 profilometer and atomic force microscopy.

Synthesis of β -NaYF₄: 3% Er, 17% Yb Nanoparticles. NaYF₄: 3% Er, 17% Yb nanoparticles were synthesized according to a previously published procedure,²⁹ with slight modifications to increase the dryness of the reaction mixture. Typically, 0.4 mmol of Y(CH₃COO)₃, 0.085 mmol of Yb(CH₃COO)₃, and 0.015 mmol of Er(CH₃COO)₃ were dissolved in 6 mL of oleic acid. The mixture was held at 100 °C under a vacuum for 60 min to purge oxygen and water. The fluoride-containing solution was prepared by dissolving 1 mmol of CH₃COONa and 2 mmol of NaF in a solvent mixture of 2 mL of oleic acid and 10 mL of 1-octadecence. The mixture was kept at 100 °C under a vacuum (200 mTorr) for 30 min, with periodic purging with Ar. The fluoride solution was then heated under Ar to 320 °C within 10-15 min.; the solution became clear and homogeneous at temperatures above 240 °C. The lanthanide solution was then injected into the fluoride solution within 1 min, and the resulting homogeneous, single-phase reaction mixture was maintained at 320 °C for 30 min under Ar and then allowed to cool to room temperature. The reaction was quenched by toluene, and the nanoparticles were precipitated by the addition of 100 mL of acetone and isolated by centrifugation at 5000 rpm. The samples were washed with acetone at least three times and dried in a vacuum oven at room temperature. The identity and phase purity of the product was verified by powder XRD measurements. (See Supporting Information.) TEM images of the NaYF₄: 3% Er, 17% Yb nanocrystals were obtained using an FEI Tecnai Spirit

with an acceleration voltage of 120 kV. The size of the nanocrystals obtained, as determined by TEM, is 64.6 \pm 6.1 nm, which is more uniform and slightly smaller than we had obtained previously (72 nm),²⁹ possibly as a result of our improved drying techniques for the reaction mixture.

Deposition of Thin Films of β-NaYF₄: 3% Er, 17% Yb Nanocrystals in PMMA. One hundred milligrams of NaYF₄: 3% Er, 17% Yb nanoparticles and 100 mg of PMMA (average weight = 350000 g/mol) were dissolved in 10 mL of chloroform (CHCl₃) and 2 mL of toluene with vigorous stirring. The β -NaYF₄: 3% Er, 17% Yb–PMMA thin films were prepared by spin-coating (3500 rpm) 1 drop of this solution on a glass slide or gold substrate.

Reflectivity Measurements. The NIR reflectivity of the patterned gold surface, and the adjacent smooth-gold substrate, was measured at the National Renewable Energy Laboratory (NREL) using a Continuum infrared microscope coupled to an FTIR spectrometer (Nicolet 6700) with a MCT (HgCdTe) detector and a CaF₂ beamsplitter. The sample was illuminated with white light from a quartz—halogen source. Measurements were taken in microreflectance mode with a 100 μ m square aperture. The reported spectra are averages of 128 scans with a system resolution of 4 cm⁻¹.

Confocal Upconversion Luminescence Microscopy. Confocal upconversion luminescence images were acquired using a customer-modified commercial scanning confocal Raman instrument (Aramis, Horiba Jobin Yvon) at the University of South Dakota (USD) as well as a custom-built instrument at South Dakota School of Mines and Technology (SDSM&T). Both instruments use a 980 nm continuous wave diode laser as an excitation source and capture the entire visible spectrum at each spatial point in the scan. In the modified Aramis system, the nearinfrared laser (Thorlabs) is guided through a neutral density filter and reflected by a holographic NotchPlus filter (Kaiser Optical System, Inc.) into the microscopic objective. A 50 \times objective (Olympus, MPlan NA 0.75) was used to achieve a laser-spot diameter of less than $2 \mu m$ on the sample. The sample was placed on a piezo XYZ mapping stage (200 \times 200 \times 200 μ m travel range) and scanned during the experiments. Upconversion emission was collected with the same objective and guided though the NotchPlus filter, a pinhole (500 μ m diameter), and a slit $(200 \,\mu\text{m})$ into a 460 mm spectrograph. A multichannel thermoelectric cooled (-70 °C) 3 megapixel CCD camera was used to collect the emission spectra.

The custom-built system at SDSM&T consists of a closedloop piezoelectric stage and high numerical aperture (Olympus UPLFLN-60X 0.9 NA) optics, epi-illuminating the sample with 980 nm light from a diode laser (Thorlabs), and collecting the subsequent upconverted light in shared-aperture mode. The resulting visible luminescence is separated from the excitation via a dichroic mirror and imaged at the input of a 0.64 m single grating spectrometer (150 lines/mm). The sample is raster scanned, and spectra are collected at an array of points (typically 40 × 40 pixels). Resulting images can be formed at each of the 1340 select energies sampled by the imaging CCD (Princeton Instruments SPEC-10) or averaged over a user-defined energy band.

Characterization of Patterned Gold Substrates and Upconversion Thin Films. Atomic force microscopy (AFM) images of the patterned gold surfaces, both with and without nanoparticle/PMMA films, were measured using a Nano-R2 from Pacific Nanotechnology in close-contact mode. The thickness of the nanoparticle/PMMA films was determined using AFM. Scanning electron microscopy (SEM) images of the patterned gold surfaces were acquired using a Hitachi SEM S-3400N.

RESULTS AND DISCUSSION

The active metal surfaces used in this work are two-dimensional arrays of cylindrical gold nanopillars arranged in a square lattice on a smooth gold surface. Surface plasmon polaritons (SPP) are excited when the reciprocal lattice vector satisfies the mismatch between the wave vector of the incident wave and that of the surface plasmon. The active array was designed and analyzed by the full-wave 3-D finite difference time domain (FDTD) method using EM Explorer. The surface plasmon dispersion characteristics were used to determine the initial spatial period of the nanopillar array which was used as a starting point for optimization. The period, diameter, and thickness of nanopillars were then varied in order to find the optimum geometrical parameters for maximum field enhancement at the desired 980 nm excitation wavelength. The lattice structure which exhibited minimum specular reflectance and maximum electric-field enhancement was chosen for fabrication. Details of the simulation and analysis leading to the design of the active surfaces used herein have been previously described.^{52,53}

The top image in Figure 1 shows a SEM micrograph of the rectangular lattice of holes, created using electron beam lithography, in PMMA photoresist on a 100 nm thick gold film. The bottom image in Figure 1 is a SEM micrograph of gold nanopillars on a continuous gold surface created by deposition of a 70 nm gold layer over the patterned photoresist, followed by liftoff of the photoresist. The nanopillars are 315 nm in diameter, with a periodicity of 618 nm. The patterned areas are $100 \times 100 \,\mu$ m on gold-coated 1×1 cm glass or silicon substrates. Most of the substrates used contained multiple patterned areas.

The inset in the top of Figure 1 graphically depicts the simulated spatial distribution of the electric-field intensity, E^2 , around a single nanopillar in the xz-plane with an incident planewave excitation of 980 nm wavelength and x-polarization of electric field. The simulation included a dielectric medium, representing PMMA, over the patterned gold nanopillars. The electric-field intensity around the edges of nanopillars is enhanced by more than 100-fold relative to the incident field. This enhancement is based on both the polarization of nanopillars (localized plasmons) and propagating surface plasmon polaritons. 5^{2-54} It has been noted previously that plasmonic surfaces with localized and propagating surface plasmons can be efficient substrates for luminescence enhancement.^{38,55} The average electric-field intensity within the volume of the PMMA layer was calculated by averaging the intensity of the electric field of each Yee's cell. Relative to a completely reflective surface, the patterned surface enhanced the average electric-field intensity by $11 \times$ for a 150 nm thick PMMA layer. The intensity enhancement actually achieved, however, is sensitive to the angle of incidence, wavelength, and the degree of definition of the nanopillar edges.

Figure 2 shows 2D and 3D representations of an $8 \mu m \times 8 \mu m$ atomic force microscopy (AFM) scan of gold nanopillars on a continuous gold surface prior to spin coating. A line profile of height vs scan distance is shown for the row of nanopillars marked with a shaded rectangle in the 2D image. The average nanopillar height for this sample was 69.7 \pm 0.9 nm.

Figure 3 shows 2D and 3D representations of a 10 μ m × 10 μ m AFM scan of the patterned gold surface after spin-coating



Figure 1. (Top) SEM image of the rectangular lattice of holes in PMMA photoresist on a 100 nm gold film created using electron beam lithography. (Bottom) SEM image of gold nanopillars on a continuous gold surface created by deposition of a 70 nm gold layer over the patterned photoresist, followed by lift-off of the photoresist. The nanopillars are 315 nm in diameter, with a periodicity of 618 nm. (Inset) Intensity of the electric field around a single nanopillar relative to incident intensity.

with a film of β -NaYF₄: 17% Yb, 3% Er nanocrystals in PMMA. The thickness of the upconverting film on the smooth, unpatterned areas is 89 nm as determined by AFM. (See Supporting Information.) The average size of the nanocrystals in the PMMA film is 64.6 \pm 6.1 nm. Horizontal height profiles of the AFM image at lines marked as "1" and "2" on the AFM image in Figure 3 are shown in the lower segment of Figure 3. "Height Profile 1" corresponds to a height profile for a line drawn across the tops of the gold nanopillars. "Height Profile 2" corresponds to a height profile for a line drawn between two rows of the gold nanopillars. (Note: The absolute scale for the two height profiles in Figure 3 is rather arbitrary and is not relative to the smooth gold surface. As noted previously, the top surface of the PMMA film is 89 nm above the unpatterned surface.) The AFM data clearly show that the upconverting layer coats smoothly over the patterned section of the surface. The thickness of the film between the pillars, as demonstrated by "Height Profile 2," is the same as that over the unpatterned, smooth-gold surface. "Height Profile 1" shows that upconverting film is thin enough for its surface to be affected by the underlying pillars, although the pattern is much less distinct compared to Figure 2. On the basis of the AFM data, we estimate that the thickness of the film coating over the top surfaces of the pillars ranges from



Figure 2. (Top) 2D and 3D images of an 8 μ m × 8 μ m AFM scan of gold nanopillars on a continuous gold surface. (Bottom) Horizontal height profile for row of nanopillars marked in the 2D image. Average nanopillar height for this sample is 69.7 ± 0.9 nm.



Figure 3. (Top) 2D and 3D AFM images (10 μ m × 10 μ m) of patterned gold surface spin coated with a thin film of upconverting nanoparticles (β -NaYF₄: 17% Yb, 3% Er) in PMMA. (Bottom) Horizontal height profiles of AFM image taken at points "1" and "2." "Height Profile 1" corresponds to a line drawn across the tops of the gold nanopillars. "Height Profile 2" corresponds to a line drawn between two rows of the gold nanopillars.

approximately 20 to 50 nm. A zoomed-in AFM scan of the coated patterned surface clearly shows the presence of nanoparticles in the vicinity of the pillar tops. (See Supporting Information.)

Figure 4 compares the reflectivity of the coated patterned gold surface (see Figure 3) to that of the coated, adjacent, smoothgold substrate. As predicted by FDTD simulations, the patterned surface shows reduced reflectivity in the NIR region, with a minimum reflectivity at 998 nm. The observed minimum is slightly red-shifted from the predicted value, but the 980 nm laser excitation wavelength still falls well within the extinction band. The apparent fall off in reflectance at the short-wavelength end



Figure 4. Reflectivity spectra of patterned gold surface (blue) and adjacent smooth gold surface (red) spin-coated with a thin film of upconverting nanoparticles (β -NaYF₄: 17% Yb, 3% Er) in PMMA.



Figure 5. Energy level diagram illustrating the mechanism of upconversion of NIR excitation to green and red emission in NaYF₄: Er, Yb.³²

of the spectra is due to the approaching limit of the system response.

β-NaYF₄:Yb, Er is the most efficient upconversion material reported to date, and the mechanism of NIR-to-visible upconversion in this system has been studied in detail. NIR excitation at 980 nm produces both green and red luminescence, centered at approximately 540 and 660 nm, respectively. Figure 5 illustrates the relevant UC mechanism in terms of the energy level diagrams of Er³⁺ and Yb³⁺ within the [Xe]4fⁿ electron configuration.³² The Yb³⁺ ions act as sensitizers and are the primary absorbers of the NIR excitation. The Er³⁺ ions are the activators, with the green and red luminescence corresponding to the ²H_{11/2}, S_{3/2} → ⁴I_{15/2} and ⁴F_{9/2} → ⁴I_{15/2} transitions, respectively. The luminescent states of Er³⁺ are excited via two consecutive Yb³⁺ → Er³⁺ energy transfer events, with the first energy transfer to Er³⁺ in the ⁴I_{15/2} ground state, and the second energy transfer to Er³⁺ in a long-lived intermediate excited state (i.e., ⁴I_{13/2} or ⁴I_{11/2}).

In the confocal upconversion luminescence scans presented herein, we are interested in isolating the intensity variations resulting from the interactions between the nanocrystals and the plasmonic field of the patterned gold surface. It is important, therefore, to reduce, to the greatest extent possible, intensity variations which are intrinsic to the upconverting thin film. We had previously observed significant inhomogeneity in the confocal images of the NIR-to-visible UC from our nanocrystal— PMMA films on glass slides, due to the presence of nonstatistical nanocrystal aggregates in the film.²⁹ (By "nonstatistical," we mean that the aggregates were too large and too frequent to be



Figure 6. (Top) TEM image of a thin film of β -NaYF₄: 17% Yb, 3% Er nanoparticles in PMMA spin-coated onto a copper TEM grid. (Bottom) Confocal scan of the NIR-to-green upconversion luminescence from the same film spin coated onto a glass slide. The distribution of pixel-intensity values is shown in the inset.

explained in terms of a random association of particles.) We have subsequently refined our methods (described herein) to produce thin films of PMMA containing very homogeneous distributions of nanocrystals. The upper segment of Figure 6 shows a transmission electron microscope (TEM) image of a thin film of β -NaYF₄: 17% Yb, 3% Er nanoparticles in PMMA spin-coated onto a copper TEM grid. The distribution of nanocrystals is homogeneous and lacks the large aggregates observed in earlier work. The bottom segment of Figure 6 shows a 20 μ m \times 20 μ m confocal scan of the NIR-to-green upconversion luminescence of the upconversion thin film spin coated on a glass slide. The area of each pixel in the scan corresponds to $1 \,\mu m^2$. The luminescence intensity from the film is quite homogeneous, with an average pixel value of 33.3 ± 0.6 (arbitrary units), with the observed standard deviation being only 1.8% of the average intensity value. A histogram of the distribution of pixel intensity values in the confocal scan is shown in the inset of the scan image. We note that the homogeneity of the confocal image is even greater than one would predict based on the variation in nanocrystal number density seen in the TEM image within any random $1 \,\mu\text{m}^2$ area, which probably reflects the influence of the TEM grid on the film quality and nanocrystal distribution.

The upper left segment of Figure 7 shows a bright-field optical image of a coated patterned gold surface in which an unpatterned section of the substrate is also visible. The entire surface has been spin-coated with a thin film of UC nanocrystals in PMMA



Figure 7. (Upper left) Bright-field optical image of a patterned gold surface showing the boundary with the smooth gold surface. (Upper right) Confocal image of visible upconversion luminescence formed by scanning across the edge of the patterned array of nanopillars, such that half the image is within a patterned area and half the image is over the smooth gold surface. (Bottom) Visible upconversion luminescence spectra taken from points A and B on the confocal image.

(see Figure 3). As an indication of the high quality of the UC film, we note that the presence of the UC film on the gold surfaces cannot be discerned in the optical images. The upper right section of Figure 7 shows a confocal image formed by scanning across the edge of the patterned array of nanopillars, such that half the image is within a patterned area and half the image is over the smooth gold surface. The influence of the patterned surface on the upconversion intensity is striking, and the patterned area is clearly distinguishable from the unpatterned area. The relative enhancement of upconversion emission from the patterned area is $2.5 \times$. The intensity is relatively uniform within each of the two areas, but much more so for the smooth surface relative to the patterned area. Sample UC spectra taken from the patterned (point A) and unpatterned (point B) areas of the confocal scan are shown in the lower section of Figure 7. The green and red upconversion luminescence is associated with the ${}^{2}H_{11/2}$, ${}^{4}S_{3/2} \xrightarrow{1} {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \xrightarrow{1} {}^{4}I_{15/2}$ transitions of Er^{3+} , respectively. The spectra are not corrected for instrument response and underestimate the relative intensity of the green luminescence.

In order to isolate the source of the effect of the patterned surface on NIR-to-visible upconversion, it is important to consider the influence that the relative reflectance and scatter from the two areas may have on the collected luminescence. At the maxima of the green and red upconversion emission peaks, the patterned areas are 1.55 and 1.22 times less reflective, respectively, compared to the unpatterned surface. (See Supporting Information.) We conclude, therefore, that the enhanced upconversion luminescence observed from the patterned areas is not due to increased reflectance but rather is attributable to the plasmonic properties of the surface.

To characterize further the nature of the enhancement, confocal upconversion images were acquired over a range of laser excitation powers, and the relative effect of the patterned surface on the green and red components of the visible upconversion emission was isolated. The confocal scans were again acquired at the boundary of the patterned surface, such that each image contains emission from both patterned and smooth areas. The same sample area was scanned using laser powers of 3, 6, 12, and 24 mW at 980 nm. Figure 8 shows the results of the scans obtained using excitation powers of 6 mW (top row) and 24 mW (bottom row). For each image shown in Figure 8, the left side corresponds to the patterned surface, whereas the right side is from the smooth gold. For each excitation power, images were generated based on the green upconversion intensity (first column of images in Figure 8), the red upconversion intensity (second column), and the intensity ratio of green-to-red emission (last column). The average intensity within the patterned and unpatterned areas was obtained by averaging all pixel intensities within the area of interest. The relative enhancement of the green and red upconversion emission, comparing the average intensities of the patterned to the smooth areas, is reported in Table 1 for each laser excitation power. The corrected enhancement factors given in Table 1 account for the difference in the relative reflectivity of the patterned and smooth surfaces.

There are several interesting aspects regarding the results shown in Figure 8 and Table 1. First, the right-hand column of images in Figure 8 shows the ratio of intensities of the green upconversion to that of the red. It is clear that this ratio is lower within the patterned area. This observation is consistent with the reflectance data, which shows that the reflectance of green light is more attenuated, relative to the smooth surface, than that of red light. In fact, the difference in the ratio of green-to-red upconversion can be completely accounted for by the difference in reflectivity of the two surfaces, which should reduce the greento-red ratio from the patterned surface by a factor of 0.79 relative to the smooth surface. This implies, therefore, that the green and red upconversion emissions are equally enhanced in terms of the intrinsic emission from the upconversion material. This is clear in Table 1, which shows that the corrected enhancement factors for the green and red upconversion are essentially identical.

The second interesting aspect of the data, referring again to Table 1, is that the degree of enhancement is largely insensitive to laser excitation power over the range of powers used here. There is, however, a slight, but consistent, trend of decreasing enhancement with increasing laser power, with the intrinsic enhancement factor ranging from 3.4 (3 mW excitation) to 3.1 (24 mW excitation).

If enhancement is occurring via a plasmonic intensification of the excitation field, the degree of enhancement obviously will be affected by the dependence of UC intensity on excitation power. At low excitation power densities, P, the intensity of steady-state UC luminescence is proportional to P^n , where *n* is the number of photons involved in the upconversion mechanism. It is wellknown that, at higher excitation powers, the observed UC power dependence falls below P^n , eventually exhibiting a linear dependence in the so-called "high-power limit".⁵⁶ In a previous investigation using confocal imaging to characterize our upconversion thin films on glass substrates at Argonne National Laboratory, we determined that our images were being acquired in the highpower limit, with the UC emission showing a linear dependence on excitation power.²⁹ This occurred because, although the absolute laser powers were low, the extremely tight focus of the excitation source resulted in high power densities. It is, therefore, important to determine the power dependence of UC emission for the set of experiments represented in Figure 8 and





Figure 8. Confocal images (20 μ m \times 20 μ m) of the integrated intensity of the green (first column), red (second column), and green/red (third column) upconversion emission from a thin film of β -NaYF₄: 17% Yb, 3% Er nanoparticles in PMMA spin-coated over the patterned gold surface. Each image is taken at the boundary of patterned (left) and smooth (right) surface. The upper row images (A, B, C) and bottom row (D, E, F) were acquired using 6 and 24 mW of excitation power, respectively.

Table 1. Enhancement Factors for Green and Red Upconversion Luminescence from Thin Films of β -NaYF₄: 17% Yb, 3% Er Nanoparticles in PMMA Spin-Coated over the Patterned Gold Surface, Relative to the Smooth Gold Surface (See Figure 8).^{*a*}

				corrected	corrected			
	laser power	green UC	red UC	green UC	red UC			
	(mW)	enhancement	enhancement	enhancement	enhancement			
	3	2.21	2.78	3.42	3.39			
	6	2.16	2.74	3.35	3.34			
	12	2.07	2.63	3.21	3.21			
	24	2.00	2.52	3.10	3.07			
c	^a The corrected enhancement factors account for the reduced reflectivity							

of the patterned surface relative to the smooth surface.

Table 1. Figure 9 shows a plot of the log of UC intensity for the red and green emission versus the log of laser excitation power, for both the patterned and smooth surfaces. In the low-power limit, the slopes of the plots should correspond to the number of photons, *n*, involved in the UC mechanism, which, in this case, should be 2. (We note that a three-photon process can also contribute to red emission, so that the observed slope can be greater than 2 over certain power ranges.^{32,57})

The observed slopes shown in Figure 9 demonstrate that the data in Figure 8 and Table 1 were acquired below the high-power limit, although the power densities appear to be above the lowpower regime, given that the slopes are less than 2. The observed power dependence, x (with x < n), is similar for the patterned and smooth surfaces. The increased slope for the red emission relative to the green could be attributed to a contribution from a three-photon process.^{32,57} We note that, although we have fit



Figure 9. Plots of the log of upconversion intensity vs log of laser excitation power for the green (upper plot) and red (lower plot) UC emission from both the patterned and unpatterned gold surfaces corresponding to the sample areas shown in Figure 8. Laser power is in milliwatts.

the log (intensity) versus log (laser power) data to a line, there is a slight curvature to the data, indicating a decrease in slope with increasing laser power. This is consistent with the observation that the enhancement factors in Table 1 decrease slightly with increasing laser power. If the enhancement mechanism involves amplification of P, the enhancement factor should be proportional to $(P'/P)^x$, where P' and P are the power densities on the



Figure 10. Distribution of pixel intensities for green upconversion emission within the confocal image shown in Figure 8 for 6 mW laser excitation power for the entire image (upper plot) and the patterned and unpatterned areas (lower plot). No corrections have been made for the different reflectivity of the green emission by the patterned and unpatterned surfaces.

patterned and smooth surfaces, respectively. As x decreases with increasing power, so should the enhancement factor.

If we consider the average corrected enhancement factor in Table 1 in conjunction with the observed power dependence shown in Figure 9, the implication is that the average excitation field strength within the patterned area is approximately twice that over the smooth surface (assuming that all other enhancing or quenching processes are equal for both areas). Because the field amplification is inhomogeneous within the pattern area (see inset of Figure 1), the field strength experienced by a given UC nanocrystal would depend on its position relative to the patterned surface, both vertically and laterally. Therefore, at the microscopic level, a range of enhancement factors should be observed within the patterned area. An advantage of the confocal imaging technique is that it provides a large set of intensity data over the entire surface area of the scan, so that one can analyze the distribution of intensities within any given area.

Figure 10 shows the distribution of pixel intensities for green UC emission within the confocal scan corresponding to the confocal image in Figure 8 for 6 mW laser power. The upper plot in Figure 10 shows the intensity distribution for the entire image, whereas the lower plot shows separately the intensity distributions within the patterned and unpatterned areas, respectively. The border region between the two areas is omitted from the lower plot. First, in comparing the intensity distribution over the entire image to that within the separate areas, it is clear that there is essentially no overlap of the intensity distributions of the patterned and unpatterned areas. Second, whereas the intensity distribution within the smooth area is narrow and symmetrical, the distribution within the patterned area is much broader and asymmetrical, with a tail extending out on the high-intensity side. The explanation for this is that the intensity variation within the smooth areas is due to the random distribution of nanocrystals within the PMMA film (see Figure 6). Within the patterned areas, the average intensity is increased by the amplification of the excitation field, and the

spatial variation of the excitation field intensity broadens the distribution of intensities observed.

CONCLUSIONS

An engineered plasmonic gold substrate has been used to enhance NIR-to-visible upconversion luminescence from a thin film of PMMA embedded with β -NaYF₄: 3% Er³⁺, 17% Yb³⁺ nanocrystals. Confocal imaging of the upconversion luminescence clearly distinguishes the plasmonic patterns on the substrate from the adjacent smooth gold surface. The excitation powers used were below the high-power limit, but the dependence of upconversion intensity on laser power was less than quadratic, indicating that one or more steps in the upconversion mechanism was approaching saturation. The relative upconversion enhancement decreases slightly with increasing laser power, correlating with the observed reduction in the power dependence of the upconversion process. After correcting for the difference in the relative reflectivity of the patterned and smooth gold surface, it was determined that the green and red upconversion were equally enhanced. This observation is consistent with the mechanism of enhancement being the increased excitation rate of Yb^{3+} as a result of the amplified NIR field.

The broad distribution of UC intensity observed within the patterned area, relative to that in the unpatterned area, is also consistent with the expected variation of field strength over the plasmonic surface. At the lowest laser powers used, the intrinsic enhancement factor of UC by the plasmonic substrate was 3.4. In the absence of other quenching or enhancing processes, this enhancement factor would imply an amplification of the excitation power by approximately 2. According to FDTD simulations, the average amplification of excitation intensity within the volume of the film, relative to a smooth gold surface, is approximately 11. However, the actual amplification achieved will be affected by the angle of incidence of the radiation and by the extent to which the pillar edges are sharply defined. Also, the observed enhancement is influenced by any quenching effects the patterned surface might exhibit.

The results of this study demonstrate that it is feasible to use engineered plasmonic surfaces to enhance NIR-to-visible upconversion luminescence from nanocrystalline systems. The use of engineered surfaces offers the possibility of much greater control of the location and distribution of local-field enhancement zones relative to plasmonic materials based on colloidal metal nanostructures. Future work will involve the characterization of the effect of the patterned surface on the kinetics of upconversion in order to elucidate both the quenching and enhancing mechanisms.

ASSOCIATED CONTENT

Supporting Information. Powder XRD pattern of UC nanocrystals, additional AFM images of UC thin film on gold substrate, and relative visible reflectance of patterned and unpatterned areas of gold substrate. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author *E-mail: smay@usd.edu.

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