Research Article

Visible Discrimination of Broadband Infrared Light by Dye-Enhanced Upconversion in Lanthanide-Doped Nanocrystals

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Optical upconversion of near infrared light to visible light is an attractive way to capture the optical energy or optical information contained in low-energy photons that is otherwise lost to the human eye or to certain photodetectors and solar cells. Until the recent application of broadband absorbing optical antennas, upconversion efficiency in lanthanide-doped nanocrystals was limited by the weak, narrow atomic absorption of a handful of sensitizer elements. In this work, we extend the role of the optical antenna to provide false-color, visible discrimination between bands of infrared radiation. By pairing different optical antenna dyes to specific nanoparticle compositions, unique visible emission is associated with different bands of infrared excitation. In one material set, the peak emission was increased 10-fold, and the width of the spectral response was increased more than 10-fold.

1. Introduction

Optical upconversion is a multiphoton process by which two or more photons are sequentially absorbed, followed by emission of radiation at a shorter wavelength. This process has potential in several applications, including diode-laser-pumped solid-state lasers [1, 2], luminescent bioassays [3–8], next-generation lighting [9], enhanced photovoltaic response [10, 11], and imaging applications to expand the effective spectral range of silicon-based detectors [12, 13].

Using the formalism proposed by Auzel [14], lanthanide-doped nanocrystals performing upconversion are defined as having three components: (1) the host material; (2) the sensitizing ion; and (3) an activator ion that emits the absorbed radiation at higher energy. The mechanism for upconversion of lanthanide (Ln^{3+})-doped nanocrystals is a probability-based event. The first step in this process is the absorption of a photon of energy, $h\nu_1$, by the sensitizer ion (see Scheme 1, (1)).

Scheme 1. Energy Transfer Processes:

In contrast to the concerted absorption of photons in a harmonic generation process, upconversion is a sequential absorption process that can occur at relatively low optical power densities ($1\text{--}10^3 \text{ W/cm}^2$ for upconversion versus $10^6\text{--}10^9 \text{ W/cm}^2$ for second harmonic generation [15]). Because the f-f transitions of Ln^{3+} ions are Laporte-forbidden [16, 17], the first excited state of the various Ln^{3+} ions (denoted Ln^{3+*}) has long lifetimes, up to the millisecond range [18]. This allows a high probability for the Ln^{3+*} ion to absorb an additional photon (Scheme 1, (2)) and emit an upconverted photon (Scheme 1, (3)) before either nonradiative relaxation (Scheme 1, (4)) or radiative recombination occurs (Scheme 1, (5)). The downside is that these Laporte-forbidden transitions have low molar absorptivity coefficients ($\epsilon \sim 0.5\text{--}5 \text{ M}^{-1} \text{ cm}^{-1}$).

The competing nonradiative relaxation (Scheme 1, (4)) can be reduced by incorporating the Ln^{3+} ions into a nanoparticle to prevent interaction of the Ln^{3+} ions with overtones of C-H and O-H stretching frequencies [19, 20], provided that a low phonon energy host material is used [21–23]. With phonon energies of 350 cm^{-1} , 600 cm^{-1} ,

and 880 cm^{-1} , respectively [22], lanthanum-fluoride (LaF_3), yttrium-oxide (Y_2O_3), and yttrium-orthovanadate (YVO_4) crystal lattices have been used for upconversion, but the vast majority of the results come from the sodium-yttrium-tetrafluoride (NaYF_4) host material with its low phonon energy of 370 cm^{-1} [23]. Recently energy clustering at sublattice level has been shown to enhance the efficiency of upconversion [6].

Although monochromatic quantum efficiency of 0.3% has been reported for upconversion in nanocrystalline NaYF_4 doped with ytterbium (Yb^{3+}) sensitizer and erbium (Er^{3+}) activator [24], the overall light capture efficiency of lanthanide-based upconverters is limited by the narrow spectral width and the low absorption cross-section of the atomic transitions. To address these issues, a dye acting as an optical antenna is placed on the surface of the nanocrystals to capture the incoming radiation more efficiently and to transfer that energy to the sensitizer ion. Ytterbium, the preferred sensitizing element for lanthanide upconversion, has an atomic absorption cross-section of $7 \times 10^{-5}\text{ L g}^{-1}\text{ cm}^{-1}$ [25] for the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition at 975 nm ($10,300\text{ cm}^{-1}$) [16, 17] and a peak having a full width at half maximum (FWHM) of absorption of 10 nm . In contrast, an organic dye commonly has an absorption cross-section of $200\text{--}400\text{ L g}^{-1}\text{ cm}^{-1}$ and an absorption FWHM of $\geq 100\text{ nm}$. Furthermore, the broad absorption width of the dye antenna and the sequential nature of the upconversion process mean that monochromatic light sources are not required.

When the distance from the optical antenna to the nanoparticle is on the order of 5 nm , the energy of the light captured by the optical antenna can be transferred to the nanoparticle by Förster Resonance Energy Transfer (FRET), a nonradiative mode of energy transfer proceeding via a short-range dipole-dipole interaction [26, 27]. The optical antenna concept has been applied to dye-induced downconversion [15, 27] and is the driving force for dye-sensitized solar cells [28]. Recently, Zou et al. [25] applied the optical antenna concept to upconversion, reporting a dye-induced upconversion with an activation bandwidth of $\sim 100\text{ nm}$ (versus $<20\text{ nm}$ for direct atomic absorption) and a 1,100-fold increase in peak upconversion efficiency.

In this work, we extend the function of the dye optical antenna to provide visible discrimination of infrared radiation. Optical antenna dyes with different infrared absorption and emission bands are coupled with specific rare-earth-doped nanoparticles having both differing activation wavelengths and differing upconverted emission spectra. This results in upconverting materials having increased spectral width, a 10-fold increase in response, and a distinctive visible emission associated with different bands of otherwise invisible light [29].

2. Materials and Methods

2.1. Materials and Synthesis of Lanthanide-Doped NaYF_4 Nanoparticles. The near infrared (NIR) absorbing dyes were purchased from several suppliers: DY-831 functionalized with N-hydroxysuccinimide (NHS) ester from Dyomics GmbH,

DyLight 800 functionalized with NHS ester from Pierce-Thermo Scientific Inc., DLS-776A (carboxylic acid) from Crysta-Lyn Chemical Co., and NIR-797 isothiocyanate and fluorescein-free acid (FIFA) from Sigma-Aldrich Co. The acetate salts of the lanthanide elements were purchased from Sigma-Aldrich Co., or from Strem Chemical Inc. All other chemicals were purchased from Sigma-Aldrich. All chemicals were used without further purification.

Lanthanide-doped NaYF_4 nanocrystals were synthesized following a modification of the hot oil procedure of Zhang [15, 30] using standard Schlenk-line techniques. Briefly, stoichiometric quantities of the acetate salts of the metal cations (Na^+ , Y^{3+} and trivalent lanthanide dopants) are converted to oleate salts by heating the acetate salts under vacuum in presence of octadecene solvent and oleic acid. A stoichiometric quantity of fluorine anion is added in the form of ammonium fluoride to create amorphous sodium yttrium fluoride. The amorphous material is converted to hexagonal crystalline form by heating the reaction mixture to greater than 300°C and maintaining the temperature for 10–100 minutes. The hexagonal crystalline material is shown in the X-ray scattering data of Supplemental Figure S1 (see Supplementary Material available online at <http://dx.doi.org/10.1155/2014/538163>) and in the high-resolution transmission electron microscope (HR-TEM) images of Supplemental Figures S2 and S3.

In a typical reaction, the acetate salts of the lanthanide elements are combined in stoichiometric ratios to yield a total of 1 mmol of lanthanides, to which 1 mmol of sodium acetate is added. The lanthanide salts and the sodium acetate are mixed with 4 mL oleic acid and 11 mL octadecene in a 50 mL flask, heated under vacuum to 120°C to form a clear solution and then cooled to room temperature. Four (4) mmol of ammonium fluoride are dissolved in 10 mL methanol and then added into the flask, immediately forming a white-colored precipitate. The solution is stirred for 30 minutes and then slowly heated to evaporate the methanol, followed by degassing with nitrogen at 100°C for 10 minutes. The solution under nitrogen atmosphere is heated to boiling at $\sim 324^\circ\text{C}$ and maintained for ~ 20 minutes. After the solution is cooled naturally, nanocrystals are precipitated from the solution with ethanol, followed by centrifuging at 4000 RPM . The particles are further purified by two cycles of dispersing the nanoparticles in toluene or cyclohexane, precipitating in two-fold excess ethanol, then centrifuging.

Unless otherwise noted, the NaYF_4 nanoparticles used in this study were synthesized with 20-minute reaction time at 324°C and a molar ratio of 1:1.2 oleic acid to lanthanides, resulting in well-formed hexagonal particles with long- and short-axis dimensions of $25 \pm 5\text{ nm}$ and $15 \pm 5\text{ nm}$, respectively, as measured by TEM. Greater reaction temperature and longer reaction times increase nanoparticle size, while the molar ratio of ligand (oleic acid) to lanthanide metals changes the ratio of the c -axis to the a - and b -axes of the hexagonal rod-like nanoparticles.

2.2. Amine Functionalization of Nanoparticles. Functionalization of the nanoparticles was accomplished by base-catalyzed hydrolysis and condensation of siloxane monomers containing amine groups for reaction with the functionalized

dye molecules [31]. The surface silanization procedure is a modified reverse microemulsion technique [32–34] in which a microenvironment is created to hold a single nanoparticle, thereby minimizing the probability of particles fusing together while the silica matrix is being formed.

A volume of 0.7 mL of surfactant (Igepal CO-520) is stirred into 40 mL of cyclohexane. Then, the mixture is added to a solution of 80 mg (approximately 0.3 mmol) of lanthanide-doped NaYF₄ oleic-acid-coated nanoparticles, which have been dispersed in 30 mL of cyclohexane. In a test tube, 0.6 mL of ammonium hydroxide (30% in water) is stirred into 3 mL of Igepal CO-520, and the solution of oleic-acid-capped nanoparticles is added. The resulting clear solution is sonicated for a minimum of 20 minutes to fully create the reverse microemulsion. Then, 0.05 mMol (50 μ L of 0.1 M solution in cyclohexane) amine-containing siloxane monomer (3-aminopropyl) trimethoxysilane (APS) is added to the reverse microemulsion of nanoparticles and stirred vigorously for two hours to form a thin silica shell. All reactions are performed at room temperature open to air. The functionalized, silica-coated nanoparticles are precipitated from the reaction mix with two times excess of ethanol, centrifuged, washed with a 50:50 mixture of deionized water and ethanol, and then centrifuged again to collect the nanoparticles. Fourier Transform Infrared (FTIR) data of Supplemental Figure S4 clearly show the evolution from oleic-acid coated particles to silane encapsulated nanoparticles but were not able to identify the amine group in the functionalized nanoparticles [35].

The NHS-functionalized DY-831 and certain other infrared dyes were susceptible to attack by the primary amine group of the functionalized siloxane APS. Alternate reagents, secondary and tertiary amine derivatives of APS—[3-(methylamino)propyl] trimethoxysilane and (3,3-dimethylaminopropyl) trimethoxysilane, respectively—were found to be sufficiently reactive to form the amide bond with linker functional group on the dye, yet not so reactive as to degrade the dye chemically. Chemical robustness of the infrared dyes in presence of the various amines was assessed by monitoring the optical absorption of the dye as a function of time after the amine is added, as is shown in Supplemental Figure S5. Details of the optical tracking technique are provided in the Supporting Information.

2.3. Dye Attachment to Functionalization of Nanoparticles. The dye antenna is attached to the nanoparticle by reacting either a carboxylic acid, isothiocyanate or NHS ester group, on the dye with an amine group on the functionalized nanoparticle to form an amide bond. Typical conditions were 100 mg of amine-functionalized nanoparticles dispersed in 10 mL of absolute ethanol combined with 300 μ L of 5 mM dye in ethanol or dimethyl sulfoxide (DMSO) solution, for an initial dye molecule-to-nanoparticle ratio of approximately 200:1. The reaction mixture is stirred for 20 minutes at room temperature for the NHS-functionalized dyes or for 1–2 hours at 35°C for the carboxylic-functionalized dyes. The nanoparticle-dye nanocomposite is washed with ethanol until the eluent is clear of nonbound dye.

Drying the nanoparticles—to measure their weight, thus measuring the reaction yields—often resulted in difficulty in recreating nonaggregated dispersions in solvent. The preferred procedure is to cascade the steps of amine functionalization and dye-attach without drying the nanoparticles. The solutions for optical measurements of dye-nanoparticle composites were empirically diluted with ethanol to achieve an absorbance of 0.2 in either 2 or 10 mm quartz cuvettes.

2.4. Optical Characterization Equipment. Upconversion measurements were performed on an Edinburgh Instruments model FS920 fluorimeter equipped with a cooled R928P photomultiplier. The diode laser light sources were single-mode devices purchased from QPhotonics LLC. The laser output was collimated or mildly focused by a C110TME-B aspheric lens from Thorlabs Inc. Spot sizes were measured by a scanning knife-edge technique in which a razor blade is translated through the laser beam at the position of the sample under test. The technique consists of placing a razor blade on a micrometer-driven translation stage and measuring the change in transmitted optical power as the razor blade is translated through the beam, from which one calculates the vertical and horizontal dimensions of the beam size. The continuous-wave laser power of 10–100 mW was measured on a Newport Corp. model 1918-C power meter with a model 818-SL calibrated silicon detector. Calculated power densities were in the range of 0.2 to 60 W/cm².

Fluorescence measurements were made on an Edinburgh Instruments model FS920 fluorimeter equipped with a cooled R2658P photomultiplier and a cooled InGaAs PIN photodiode. Absorption measurements of the dyes were made on a Perkin-Elmer Lambda 19 ultraviolet-visible-near infrared (UV/VIS/NIR) spectrophotometer.

2.5. Material Characterization Equipment. The HR-TEM images were recorded with an FEI Titan 80–300 TEM. The X-ray diffraction spectra were recorded with a Bruker AXS D8 Discover powder X-ray diffractometer. Thermogravimetric analysis (TGA) was performed on a TA Instruments model TGA-Q500 thermogravimetric analyzer.

3. Results and Discussion

3.1. Nanoparticle Synthesis and Characterization. The upconversion efficiency is strongly dependent on the crystalline phase and, to a lesser degree, on the size of the particles. No upconversion was seen from the amorphous material or from the cubic phase material, which are the dominant phases for reaction temperatures less than 300°C [30]. At reaction temperatures ranging from 300°C to 324°C, the desired hexagonal crystalline phase is formed, as is shown in the large-angle X-ray diffraction measurements of Supplemental Figure S1. Higher reaction temperature and longer reaction times increase the size of the nanoparticles, while the molar ratio of ligand (oleic acid) to lanthanide metals changes the ratio of the *c*-axis to the *a*- and *b*-axes of the hexagonal rod-like nanoparticles. The shape of the nanoparticles, as well as their well-defined hexagonal crystalline lattice, is shown in the HR-TEM image of Supplemental Figure S2. The sharp

FIGURE 1: HR-TEM images and relative upconversion efficiency illustrate the strong dependence on the reaction temperature for the properties of $\text{NaY}_{0.747}\text{Yb}_{0.25}\text{Tm}_{0.003}\text{F}_4$ nanoparticles (a). At 300°C , small particles (12 nm or less) are formed with poorly defined crystal structure. At 315°C , Ostwald ripening results in large hexagonal phase particles with high lattice uniformity (b). In both images, the scale bar equals 20 nm. Under identical measurement conditions, the upconversion intensity for the 315°C -processed particles (black curve) is more than 10 times stronger than that from the 300°C -processed material (blue curve).

patterns in the fast Fourier transform of the diffraction from a single crystal are further evidence of the well-formed hexagonal crystals.

Figure 1 shows the variation of upconversion with particle size. Larger format renderings of the TEM images are provided in Section F of the Supporting Information. The HR-TEM images show the small (≤ 12 nm) nanoparticles grown at 300°C and the large (70 nm) particles grown at 315°C . In both cases, the reaction time was 80 minutes. An Ostwald ripening process [36, 37] causes the smaller, high-surface-energy particles to dissolve, allowing the material to regrow on established nanoparticles to create larger nanocrystals having lower energy states and reduced surface defects. Figure 1 shows that, for direct atomic excitation and with all other parameters being the same, the upconversion from

the larger nanoparticles is 10 times greater than that of the smaller nanoparticles. For the upconversion by direct atomic absorption, larger particles are more efficient, due, in part, to the lesser ratio of surface sites (and surface defects) to interior volume. In the case of dye-induced upconversion, smaller nanoparticles are expected to be more efficient due to the short-range of the FRET mechanism (the Förster distance for 50% drop in energy transfer efficiency is in the range of 2–6 nm [26]). For this study, a target particle size of 15×25 nm was selected, although no specific measurements of efficiency of dye-induced upconversion versus particle size were performed.

3.2. Selection of Lanthanide Dopants and Associated Upconversion Spectra. The selection of lanthanide dopants and

their loading levels is linked to the intended upconversion pathway. In its most common embodiment, the infrared upconversion in lanthanide-doped nanoparticles is initiated by the absorption of 975 nm light by the sensitizer ion Yb^{3+} , followed by energy transfer and ladder-climbing in the manifold of states in the activator ions [5, 14, 23, 25, 30], such as erbium Er^{3+} , holmium (Ho^{3+}), and thulium (Tm^{3+}). In the material systems where the sensitizer and activator are different ions, the doping level of the sensitizing ion (Yb^{3+}) is high for two reasons: first, to capture the incoming radiation, and second, to increase the probability of energy transfer from the Yb^{3+} ion to the activator ions. On the other hand, the doping level of the activators is low to prevent self-absorption by the lanthanide-emitting elements [6, 8] and to reduce the number of sites to which energy from the sensitizing ions is transferred, thereby increasing the probability of inducing multiple-photon transfer into the activator ions. In this study, the doping levels were 20–25% for Yb^{3+} , 2% for Ho^{3+} , 2.5% for Er^{3+} , and 0.3% for Tm^{3+} . Upconversion spectra for the 975 nm diode laser excitation of NaYF_4 nanoparticles doped with combinations of $\text{Yb}^{3+}:\text{Tm}^{3+}$, $\text{Yb}^{3+}:\text{Ho}^{3+}$, and $\text{Yb}^{3+}:\text{Er}^{3+}$ are shown in Figure 2.

Additional sensitizing wavelengths besides 975 nm were required to demonstrate the discrimination of infrared light based on the absorption properties of the attached optical dye antenna. Er^{3+} , Nd^{3+} , and Ho^{3+} ions have been shown to act as both the sensitizer and the activator [10, 13, 14, 38, 39], generating upconversion for excitation at discrete wavelengths from the visible spectrum to the NIR spectrum. Figure 3 shows the characteristic upconversion spectrum of erbium for the excitation of $\text{NaY}_{0.85}\text{Er}_{0.15}\text{F}_4$ at 801 nm, 975 nm, and 1550 nm. For this class of NaYF_4 nanoparticles in which the Er^{3+} ion acts as both sensitizer and activator, the optimal doping level for Er^{3+} is around 15% [38]. Although the 1550 nm excitation offers the largest spectral window for the dye antenna, the selection of available infrared-emitting dyes dictated the use of the 801 nm excitation for our study of dye-induced upconversion.

3.3. Selection of Optical Antenna and Matching with Sensitizing Ion. The role of the optical antenna is the efficient capture of the incoming radiation and transfer of that energy to the sensitizer element in the nanoparticle. The optical requirements for the dye antenna are strong absorption in the infrared wavelength band of interest, high fluorescence efficiency at the sensitizer gateway wavelength (975 nm for Yb^{3+} , 801 nm for Er^{3+}), fast energy transfer from the dye to the active ion, and transparency (no absorption) in the visible region. Although a number of commercially available dyes meet the optical requirements, there is only a sparse selection of dyes that also have the functional group needed to bond to the nanoparticle surface. Since the operative energy transfer mechanism, FRET, drops as the inverse of separation distance to the sixth power ($1/r^6$), it is crucial to make a short linkage between the donor (the optical antenna) and the receptor (the sensitizing element in the nanoparticle). We chose to make that tight linkage with a covalent amide bond that is formed

FIGURE 2: Upconversion spectra for NaYF_4 nanoparticles doped with Yb^{3+} as the sensitizer and different lanthanide activator ions: Tm^{3+} , Ho^{3+} , and Er^{3+} , respectively, for curves from top to bottom. The infrared excitation light was from a 975 nm diode laser.

FIGURE 3: Upconversion spectra for Er^{3+} -doped $\text{NaY}_{0.85}\text{Er}_{0.15}\text{F}_4$, in which the Er^{3+} ion acts as both sensitizer and activator. Excitation at 801 nm, 975 nm, and 1550 nm (black, blue and magenta curves, resp.) results in nearly identical emission spectra with a slight enhancement of the 655 nm emission for excitation at 1550 nm.

by the reaction of a carboxylic acid, an isothiocyanate, or an NHS ester functional group on the dye antennae with an amine group on the functionalized nanoparticle.

FIGURE 4: Normalized absorption and emission spectra of the NHS-functionalized form of DyL800 dye (a) and DY-831 dye (b) in DMSO solvent. At high concentrations, these dyes appear dark green or black to the eye. At concentrations resulting in peak attenuation of 90% in the infrared, they are transparent in the visible.

Figure 4 shows the absorption and emission spectra of the principle infrared dyes used in this study, the NHS-functionalized version of DyL800 and DY-831 in DMSO solvent. The manufacturers list peak molar extinction coefficients of 220,000 and 270,000 $\text{M}^{-1} \text{cm}^{-1}$, respectively. The photograph inset in Figure 4(a) shows that these dyes appear dark green or black at high concentrations, while, at concentrations resulting in a peak infrared attenuation of >90% per cm, they appear transparent in the visible spectral region. The solution of DyL800 dye labeled “100x dilution” in the photo inset had a peak infrared absorbance of more than 2.0 in a 1 cm cell, while its average transmission from 400 to 600 nm was 85% in the same 1 cm cell. The absorption and emission measurements of the NHS-functionalized version of DyL800 (Figure 4(a)) were made in a 1 cm cell using a further approximately tenfold dilution of the solution labeled 100x dil.

The DY-831 dye was chosen for its unique broad fluorescence, which extends out to the 975 nm atomic absorption of the Yb^{3+} sensitizer. The absorption and emission bands of the DyL800 dye are narrower than those of DY-831 and are at shorter wavelengths. Dye-induced upconversion of Er^{3+} -doped nanoparticles was also achieved with NIR-797 isothiocyanate and DLS-776A infrared dyes, which have absorption and emission spectra that are substantially similar to those of DyL800 (see Supplemental Figure S6).

FRET has been reported for nanocomposites made with dyes attached by physisorption [40] by ligand exchange [25, 41, 42] and by covalent bonds [3, 15, 27]. Although all three techniques yield the desired short separation distance between dye and nanoparticle, the strong covalent bond is best able to withstand subsequent processing steps. The amide covalent bond is formed by the reaction of a carboxylic acid, isothiocyanate, or an NHS ester functional group on the as-purchased infrared dyes, with the surface amine group on the functionalized nanoparticles. The nanoparticle is functionalized by a surface silanization technique following

a modification of the method of van Blaaderen and Vrij [31] for creating dye-doped silica spheres.

Surface silanization by the hydrolysis and condensation of siloxane monomers is a general technique for coating surfaces with silica and for imparting a surface functionalization by selecting siloxane monomers that contain the desired functional groups [4, 15, 32, 33], in our case, an amine group. A thin functionalized silica shell is created by the condensation of a controlled amount of amine-functionalized siloxane monomers. Agglomeration of the nanoparticles during shell growth is reduced by the use of a reverse microemulsion [15, 32–34] process in which the size of the microemulsion is tailored to contain a single nanoparticle. Our initial goal was to minimize the distance from dye antenna to nanoparticle by first reacting the amine-functionalized siloxane monomers with the dye antenna, then condensing the covalently bonded dye-siloxane monomer onto the surface of the nanoparticle. In a second step, nonfunctionalized siloxane monomers are added to create a thicker encapsulating layer (see Supplemental Figure S3), thereby protecting the dye-antenna and creating an outer shell that can be later functionalized to promote dispersion of the nanoparticles into nanocomposite materials. This process has been demonstrated for several visible and NIR dyes [15, 31, 34], and was used in our initial test with the visible dye fluorescein-free acid (FIFA) to measure the efficiency of FRET in the more traditional case of energy flow from excited nanoparticles to the attached fluorescent dye (see Supplemental Figure S7). Unfortunately, the infrared dyes used in this study were not robust to the highly basic conditions of siloxane condensation. A modified dye-attach procedure was adopted in which the nanoparticles first undergo the base-catalyzed condensation to form a thin amine-functionalized silica shell. The thinly encapsulated particles are purified and then allowed to react with the dye under milder conditions. Drawbacks of the modified process are that it leaves the dye exposed on

FIGURE 5: TEM image $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ nanoparticles with nominal 12 nm thick silica shell ((a); scale bar is 50 nm). TEM image $\text{NaYF}_4:\text{Yb}^{3+}, \text{Ho}^{3+}$ nanoparticles with a thinner silica shell estimated to be 2 nm or less ((b); scale bar is 20 nm). In both cases, the silica shell includes the attached infrared dye, which is not discernible in the TEM image.

the surface of the silica-coated nanoparticle and results in a larger distance between dye and nanoparticle, thereby reducing the efficiency of the FRET.

The TEM image in Figure 5(b), is typical of the amine-functionalized, silica-coated particles used in this study, namely, hexagonal particles sized 25 ± 5 nm and 15 ± 5 (long and short axis, resp.). The silica shell contains the dye antenna, but neither the silica shell nor the dye that is attached to the outside of the shell is discernible in this TEM image.

The particles in Figure 5(a), have the additional nonfunctionalized silica shell mentioned above which encapsulates the inner amine-functionalized shell and the attached dye.

In the TEM image of Figure 5(a), and the end-on view in Supplemental Figure S3, the thick silica shell (nominal 12 nm thickness) appears light gray and featureless. The thinner silica shell in Figure 5(b), is not discernible in the TEM images (larger format renderings of the TEM images are provided in Section F of the Supporting Information). The presence of the silica shell is however known from the FTIR measurements. The shell thickness is estimated to be 2 nm or less. The estimate is based on geometric calculations starting with the 12 nm shell thickness on the nanoparticles of Figure 5(a), and factoring in the 100-fold lower ratio of silane reagent to nanoparticles for the reaction in Figure 5(b), and the approximately 15x lower surface area of those smaller particles. In a future experiment, the shell thickness could be better estimated by creating a series of encapsulated nanoparticles using a range of ratios of silane reagent to nanoparticles. The thickness of the resulting silica shell would be measured on the TEM for the progressively thinner shells. At some point, the silica shell will no longer be discernible in the TEM, but a plot of measured thickness versus silane reagent could be extrapolated to the conditions used in our target materials.

The TEM images of the as-sensitized nanoparticles show crisp hexagonal-shaped rods with a strong tendency for self-assembly on the TEM grid (see Supplemental Figure S2),

while the silica-coated particles show rounded contours and reduced tendency for self-assembly (Figure 5). The TEM image of nanoparticles with thick silica shells (Figure 5(a)) shows instances of a thick silica shell encapsulating two nanoparticles and of a silica sphere without a nanoparticle. The TEM image of nanoparticles with thin silica shells (Figure 5(b)) shows only individually encapsulated nanoparticles.

3.4. Measurements of Direct-Atomic and Dye-Induced Upconversion. The dye attachment process is performed by dispersing the amine-functionalized nanoparticles in ethanol and stirring in the dye at a dye molecule-to-nanoparticle ratio of 200 : 1. After the excess nonbound dye is removed by washing with ethanol, the dye coverage on the nanoparticle is calculated from the optical absorption of the dye in the dye-nanoparticle composite. The particles used in this study are the ones shown in the TEM image of Figure 5(b).

The photograph in Supplemental Figure S8 shows the color change of the dye-attached nanoparticles as coverage of the infrared dye DLS-796A increases from ~ 0.1 to ~ 100 dye molecules per nanoparticle. Up to 10% of the available dye stayed attached to the nanoparticle, while the rest was removed by repeated washing with ethanol. Based on the optical absorption measurements, dye attachment shows saturation around 60 dye molecules per 25 nm nanoparticle.

Figure 6 contrasts the atomic absorption of lanthanide-doped nanoparticles with the molecular absorption of the dye-attached nanocomposite. The black curve is the optical absorption of a colloidal solution of $\text{NaY}_{0.85}\text{Er}_{0.15}\text{F}_4$ in cyclohexane. The small average particle size of <10 nm for this batch of nanoparticles enabled the clear colloidal solution with a high particle loading of 150 mg nanoparticle in 4 mL of hexane, equivalent to a 0.14 M solution when applying the weight percent from TGA measurements (see Supplemental Figure S9). The green curve of Figure 6 is

FIGURE 6: Contrast of the atomic absorption of lanthanide-doped nanoparticles with the molecular absorption of the dye-attached nanocomposite. The black curve is the optical absorption of a colloidal solution of $\text{NaY}_{0.85}\text{Er}_{0.15}\text{F}_4$ (37 mg/mL in hexane), while the green curve is the optical absorption of 17 mg/mL solution of the nanoparticles after functionalization and reaction with DyL800 infrared dye.

the optical absorption of the same batch of nanoparticles after amine functionalization and reaction with an excess of NHS-functionalized DyL800 infrared dye. Using the manufacturer-supplied dye extinction coefficient $\epsilon = 270,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ ($260 \text{ L g}^{-1} \text{ cm}^{-1}$) and nanoparticle size measurements from TEM, calculations indicate 0.2 dye molecules per 10 nm nanoparticle, assuming 100% recovery of the initial 50 mg of nanoparticles after the repeated washing cycles.

The atomic absorptions of the $\text{NaYF}_4:\text{Er}^{3+}$ nanoparticles are annotated in the expanded view of the absorption spectrum shown in Supplemental Figure S10. From the six-time expansion (inset of Supplemental Figure S10), one calculates an extinction coefficient $\epsilon = 0.03 \text{ L mol}^{-1} \text{ cm}^{-1}$ ($1.4 \times 10^{-4} \text{ L g}^{-1} \text{ cm}^{-1}$) and a half width of $\leq 5 \text{ nm}$ for the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ atomic absorption of the Er^{3+} ion at 801 nm. In comparison, the DyL800 infrared dye has an extinction coefficient of $\epsilon = 270,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ ($260 \text{ L g}^{-1} \text{ cm}^{-1}$) and a half width of 50 nm, representing a greater than 10-fold increase in absorption width and a 10^6 -fold increase in absorption cross-section.

Figures 7 and 8 demonstrate the dye-induced upconversion of two sets of lanthanide-doped NaYF_4 nanoparticles. Figure 7 demonstrates dye-induced upconversion of nanoparticles doped with Yb^{3+} as the sensitizer and Ho^{3+} as the activator ($\text{NaY}_{0.78}\text{Yb}_{0.20}\text{Ho}_{0.02}\text{F}_4$) and with attached DY-831 dye. Plots (a), (b), and (c) show the upconversion for excitation at 801 nm, 819 nm, and 832 nm, respectively, where the DY-831 infrared dye absorbs, but where the Yb^{3+} sensitizer

FIGURE 7: Demonstration of dye-induced upconversion of NaYF_4 nanoparticles doped with Yb^{3+} sensitizer and holmium activator ($\text{NaY}_{0.78}\text{Yb}_{0.20}\text{Ho}_{0.02}\text{F}_4$). Plots (a), (b), and (c) show the emission for excitation at 801 nm, 819 nm, and 832 nm, respectively, where the attached DY-831 infrared dye absorbs, but where the Yb^{3+} sensitizer does not. Characteristic Ho^{3+} upconversion is seen in plot (d) for excitation at 975 nm. Ho^{3+} upconversion is seen in plots (a), (b), and (c) for the dye-attached nanoparticles (black curves), while none is seen for the control nanoparticles without attached dye (blue curves).

does not. The characteristic upconversion spectrum of Ho^{3+} is seen for the dye-attached nanoparticles (black curve), while no upconversion is seen for the control without attached dye (blue curve). The curves in plots (a) and (b) have a sharp feature at 801 nm and 819 nm, respectively, due to leakage of the laser light. No such feature is seen in the curves of plots (c) and (d) because an infrared blocking colored glass filter was inserted to block the scattered laser light. The same filter also reduces the intensity of emission at 645 nm. Plot (d) in Figure 7 is the reference, that is, excitation at 975 nm where Yb^{3+} absorbs ($^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$), but where the dye does not. Since the DY-831 dye does not absorb at 975 nm, similar upconversion was expected for the dye-attached nanoparticle and for the control, but results showed a 10-fold reduction of upconversion for the dye-attached particles. The hypothesis is that a residual absorption by dye in the region of 975 nm could result in a deactivation of the excited state of the Yb^{3+} sensitizer, thus decreasing the overall upconversion efficiency.

Figure 8 demonstrates dye-induced upconversion for a second material set, NaYF_4 nanoparticles using Er^{3+} as both sensitizer and activator ($\text{NaY}_{0.85}\text{Er}_{0.15}\text{F}_4$) and with attached DyL800 infrared dye. Plot (a) is for excitation at 785 nm where the DyL800 dye absorbs, but Er^{3+} does not. Plot (b)

FIGURE 8: Demonstration of dye-induced upconversion of NaYF_4 nanoparticles doped with Er^{3+} as both sensitizer and activator ($\text{NaY}_{0.85}\text{Er}_{0.15}\text{F}_4$). Plot (a) is for excitation at 785 nm where the attached DyL800 dye absorbs, but Er^{3+} does not; the characteristic erbium upconversion spectrum is seen for the dye-attached nanoparticles (black curve) while no upconversion is seen for the control without attached dye (blue curve). Plot (b) is for excitation at 801 nm where Er^{3+} absorbs, but where absorption of the dye is less.

shows the reference, that is, excitation at 801 nm, where Er^{3+} absorbs, but where absorption of the dye is less. In both cases, the black curves are for the dye-attached particles, while the blue curves are for the control nanoparticles without attached dye. The sharp features at 785 nm and 801 nm are scattered laser light. The broad feature starting around 650 nm is the emission of the DyL800 dye, which is truncated by infrared blocking filters.

For the 785 nm excitation, the characteristic Er^{3+} upconversion spectrum is seen for the dye-attached nanoparticles (black curve) while no upconversion is seen for the control without attached dye (blue curve). Even at 801 nm, which corresponds to the peak of the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ absorption of the Er^{3+} ion, the tail of the dye absorption induces an upconversion that is 10 times stronger than upconversion from the direct atomic excitation.

The excitation light came from discrete diode lasers and collimating optics, which were manually swapped and aligned for each wavelength change. To minimize errors due to alignment or beam size, upconversion measurements in Figures 7 and 8 were performed as pairwise comparisons of dye-attached nanoparticle versus bare nanoparticles. For a given diode laser operating at fixed wavelength and power density, upconversion measurements were made by swapping one sample cell with dye-doped nanoparticles for another one containing nanoparticles without attached dye.

3.5. Power Dependence of Upconversion. The power dependence of upconversion is derived from measurements of the continuous-wave optical power of the diode laser, the measurement of the laser beam size on target, and the measured integrated area under the spectral emission curve. The power of the continuous-wave diode lasers varied between 2 and 120 mW, with a nominal spot size on target of 0.15 to 0.7 mm^2 . A scanning knife-edge technique is used to measure the beam size at the position corresponding to the center of the quartz sample cell.

Figure 9(a), shows the power dependence of the upconversion of $\text{NaY}_{0.78}\text{Yb}_{0.20}\text{Ho}_{0.02}\text{F}_4$ under direct excitation at 975 nm of the atomic absorption of the Yb^{3+} activator. Upconverted power is measured as the integrated area under the spectral emission curve from 535 nm to 555 nm. Curve fitting shows the expected two-photon power dependence. Figure 9(b), shows the change in transmitted power as a function of translation distance of the razor blade, from which is calculated 0.92 mm FWHM for the horizontal dimension of the 975 nm diode laser beam at the position of the center of the sample cell. The calculated FWHM in the other scan direction was the same, within measurement error, for this fiber-coupled diode laser device.

Figure 9(c), shows the power dependence of upconversion of $\text{NaY}_{0.85}\text{Er}_{0.15}\text{F}_4$ under direct excitation at 801 nm of the atomic absorption of the Er^{3+} activator. Upconverted power is measured as the integrated area under the spectral emission curve from 520 nm to 570 nm. Curve fitting shows a near two-photon power dependence. The scanning knife-edge results shown in Figure 9(d), indicates a 0.33 mm and 0.51 mm FWHM respectively for the vertical and horizontal directions of this free-space diode laser. Depending on the operating temperature and the drive current, this diode laser exhibits either a single longitudinal mode (a single, narrow-width wavelength) or two to three longitudinal modes, that is, multiple spectral lines. Because of the narrow width of the atomic absorption of erbium near 801 nm, the wavelength of the diode laser is temperature-tuned to achieve the maximum upconverted signal from the same amount of measured continuous-wave laser power. Wavelengths vary from 800.8 nm at 15°C to 806.4 nm at 35°C, equivalent to 0.28 nm per degree Celsius. Highest upconversion is achieved at 17°C heat sink temperature, producing a wavelength of 801 nm.

Figure 10(a) shows the power dependence of dye-induced upconversion of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Ho}^{3+}$ with DY-831 dye under excitation of dye at 819 nm and 785 nm, where the dye absorbs, but the nanoparticle does not. Upconverted power is measured as the integrated area under the curve from 535 nm to 555 nm. Curve fitting shows a two-photon power dependence at 785 nm, but a fractional 1.4 power dependence at 819 nm. Figure 10(b), shows the power dependence of dye-induced upconversion of $\text{NaYF}_4:\text{Er}^{3+}$ with DyL800 under excitation of dye at 785 nm, where the dye absorbs, but the nanoparticle does not. Upconverted power is measured as the integrated area under the curve from 520 nm to 570 nm. Curve fitting shows a near two-photon power dependence. As stated earlier, the different excitation wavelengths are generated by manually swapping and collimating discrete

FIGURE 9: Power dependence of direct atomically excited upconversion of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Ho}^{3+}$ excited at 975 nm (a). Beam size measurement of the fiber-coupled 975 nm diode laser (b). Power dependence of direct atomically excited upconversion of $\text{NaY}_{0.85}\text{Er}_{0.15}\text{F}_4$ excited at 801 nm (c). Beam size measurements for the vertical and horizontal directions for the 801 nm free-space diode laser (d).

diode laser. During the measurements in Figure 10, the beam size was not measured by the lengthy scanning knife-edge technique, hence the decision to plot the data as a function of measured continuous-wave laser power. Assuming that the beam sizes on target were the same as shown in Figure 9(d),

the estimated power density in Figure 10 would be $11 \text{ W}/\text{cm}^2$ and $60 \text{ W}/\text{cm}^2$ for 20 mW and 100 mW, respectively.

The power dependence of the dye-induced upconversion indicates a two-photon process, similar to the power dependence for direct atomic excitation. Estimated quantum

FIGURE 10: Power dependence of dye-induced upconversion of NaYF₄:Yb³⁺, Ho³⁺ with DY-831 dye under excitation of dye at 819 nm and 785 nm, blue diamonds and brown squares respectively (a); Power dependence of dye-induced upconversion of NaYF₄:Er³⁺ with DyL800 under excitation of dye at 785 nm (b).

efficiency is less than 10^{-4} , well below the values reported by Zou et al. [25]. One explanation for the reduced efficiency is the larger separation between dye and nanoparticle caused by our modified dye-attach process that was necessitated by the chemical fragility of the dye molecules.

Taken together, this data is a clear indication that energy transfer from the dye is the source of the upconverted signal. Demonstration of dye-induced upconversion was done with four discrete diode lasers, but it should be possible with any wavelength in the absorption band of the dye. Within the constraints of the discrete excitation wavelengths, the data also show that the two material sets have different responses depending on the wavelength of the incoming infrared excitation, and that they produce spectrally different visible emissions.

4. Conclusions

In summary, dye-induced upconversion was demonstrated for two nanocomposite systems with different optical antenna and different lanthanide-based upconversion pathways. Infrared fluorescing dyes were closely bound to the nanoparticles and acted as efficient light-harvesting optical antennae for the upconversion process in lanthanide-doped NaYF₄. The different upconversion pathways emanate from two different activation wavelengths: 801 nm for Er³⁺ in the NaYF₄:Er³⁺ system and 975 nm for the Yb³⁺ sensitizer in codoped NaYF₄:Yb³⁺, Ln³⁺ (Ln = Ho, Tm, Er, etc.). Discrimination of different bands of infrared light radiation was demonstrated by specific pairing of dye antennae having different infrared absorption bands with nanoparticles having both different activation wavelengths and visibly different upconverted emission. Practical applications of this technique include extending the wavelength range of silicon solar cells [10, 11] and providing a visible laser threat warning [29]. Individual diode lasers were used to demonstrate dye-induced upconversion at four discrete wavelengths. Similar

results are expected for any wavelength in the absorption band of the dye. In the preferred configuration, the dye optical antenna provided a greater than 10-fold increase of effective spectral width for upconversion, and a 10-fold increase in the monochromatic upconversion efficiencies, as compared to upconversion by direct atomic absorption.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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