Published in final edited form as:

Nanotechnology. 2011 August 12; 22(32): 325604. doi:10.1088/0957-4484/22/32/325604.

Upconversion in NaYF₄: Yb, Er Nanoparticles Amplified by Metal Nanostructures

Wei Deng¹, L. Sudheendra², Jiangbo Zhao¹, Junxiang Fu³, Dayong Jin¹, Ian M. Kennedy², and Ewa M Goldys^{3,4}

¹Department of Physics and Astronomy, Macquarie University, North Ryde 2112 NSW, Australia

²Mechanical and Aeronautical Engineering, University of California, Davis, CA 95616-5294, USA

³Department of Chemistry, University of California, Riverside, CA 92521, USA

Abstract

Upconversion (UC) fluorescence in NaYF₄: Yb, Er nanoparticles amplified by metal nanostructures was compared in two nanostructure geometries: gold nanoshells surrounding nanoparticles and silver nanostructures adjacent to the nanoparticles, both placed on a dielectric silica surface. Enhanced UC luminescence signals and modified lifetimes induced by these two metals were observed in our study. The UC luminescence intensities of green and red emissions were enhanced by Ag nanostructures by a factor of approximately 4.4 and 3.5, respectively. The corresponding UC lifetimes were reduced ~1.7-fold and ~2.4-fold. In NaYF₄: Yb, Er nanoparticles encapsulated in gold nanoshells, higher luminescence enhancement factors were obtained (~9.1-fold for the green emission and ~6.7-fold for the red emission). However, the Au shell coating extended the red emission by a factor of 1.5 and did not obviously change the lifetime of green emission. The responsible mechanisms such as plasmonic enhancement and surface effects are discussed.

1. Introduction

Lanthanide-doped upconverting (UC) nanocrystals have recently emerged as an area of intense research activity, due to their potential applications in life sciences research and security [1–4]. In contrast to the conventional inorganic fluorophores [5–6], organic dyes [7–8], and semiconductor quantum dots [9–10], these nanoparticles use inexpensive and high-power near-infrared (NIR) diode lasers as the excitation source to produce visible luminescence. Under continuous-wave excitation at 980 nm, the particles exhibit superior photostability and unique up-conversion (UC) luminescence that has many attractive features, such as sharp absorption and emission lines with full width at half maximum of 15 nm [11]. Furthermore, upconversion is excited in NIR which minimizes possible photodamage in biological systems, it limits the excitation of autofluorescence and it permits deeper tissue penetration for bio-imaging [12–13]. Despite these advantages, the nanoparticles typically have low emission efficiency due to surface quenching, particularly strong in small nanoparticles with large surface area/volume ratio and a relatively small photon absorption cross section. Intense research efforts are currently directed towards maximizing UC quantum yield [14–15] often by searching for optimum combinations of different host matrices and rare-earth (RE) atoms.

⁴Author to whom any correspondence should be addressed. ewa.goldys@mq.edu.au.

In this work we explored two alternative strategies to achieve enhanced luminescence, by the addition of different noble metals in proximity to UC lanthanide nanophosphors. The comparison serves to elucidate some of the underlying mechanisms that underpin metal enhancement of emission from this class of materials. The nanoscale fluorophore-metal interactions give rise to the process known as metal-enhanced fluorescence (MEF) [16–19]. The MEF effect is due to excited fluorophores interacting with surface plasmon resonances in metals; this effect is particularly strong in metal nanostructures. MEF has been shown to produce desirable effects such as increased quantum yield of fluorophores, their decreased lifetimes, increased photostability, and potential for improved energy transfer [16]. Due to the above advantages, MEF has been widely used for fluorescence enhancement from organic dyes [20–21] rare-earth complexes [22–23], and quantum dots [24–25]. Among different MEF substrates, silver and gold are the most widely investigated materials due to their unique plasmonic properties, such as surface plasmon resonances in the visible wavelength range [26]. Recently, the coupling of UC materials with metal nanomaterials (Ag and Au) has been reported, mainly focusing on Er in glass composites and film [27–29]. Such films are, however incompatible with biological applications. To the best of our knowledge, there have been no reports that demonstrate and compare the metal-enhanced UC luminescence achieved through the use of both silver and gold nanostructures with different morphologies.

In this study we demonstrate metal-induced enhancement of the UC luminescence of NaYF₄: Yb, Er nanoparticles in two different experimental systems. In the first system the nanoparticles were made water-soluble by deposition of a thin silica coating. Further, they were conjugated to silver nanostructures deposited on the surface of dielectric silica beads. The silica coating additionally ensured nanoscale separation between nanoparticles and metal nanostructures, which is required to prevent metal quenching. The conjugation was achieved by using a simple bioassay, where streptavidin (SA)-labeled UC nanoparticles were bound to the biotinylated anti-mouse IgG antibody. This assay was carried out on silica beads with and without Ag nanostructures under the same experimental conditions to permit a valid comparison of effectiveness. The Ag nanostructures on silica beads had a broad absorption band around 400 nm. In the second system, the NaYF₄: Yb, Er nanoparticles were coated with ~5–8 nm thick gold shells [30]. The gold nanoshells had a strong absorbance in the green region of the visible spectrum and they did not inhibit emission from Er³⁺ centered around 525 and 545 nm. This is in direct contrast to the case of quantum dots, where the fluorescence emission from the quantum dots is quenched by the gold shell in the core-shell architecture [31].

2. Experimental details

2.1. Materials

The following materials were purchased from Sigma-Aldrich and used as received: YCl₃ (99.9%), YbCl₃ (99.9%), ErCl₃ (99.9%), oleic acid (OA, 90%), octadecene (ODE, 90%), methanol, NaOH, NH₄F, ethanol, acetone, chloroform, CO-520, cyclohexane, hexane, tetraethyl orthosilicate (TEOS), ammonia (wt 30%), NaF (99%), HCl (36.5–38.0%), HAuCl₄, trisodium citrate, NaBH₄, (3-aminopropyl) trimethoxysilane (APTMS), concentrated H₂SO₄, silver enhancing solution A, silver enhancing solution B (enhancing kit), biotinylated rabbit anti-mouse IgG antibody, streptavidin (SA), glutaraldehyde, bovine serum albumin (BSA), phosphate buffered saline (PBS, pH 7.4), Tween 20 and poly-L-lysine. 400 nm silica beads were purchased from Bangs Laboratories, Inc. Glass microscope slides were obtained from Fisher Scientific. Nanopure water (>18.0 MΩ), purified using the Millipore Milli-Q gradient system, was used in all the experiments.

2.2.Preparation of SiO₂-coated NaYF₄: Yb, Er nanoparticles (first experimental system)

The SiO₂-coated NaYF₄: Yb, Er nanoparticles were first synthesized by thermal decomposition of rare-earth/sodium chloride precursors and the fluoride reagent in oleic acid and octadecene, then coated with the SiO₂ shell via the hydrolysis of TEOS in a basic solution [32]. First, YCl₃, YbCl₃ and ErCl₃ were mixed with OA and ODE, and this solution was heated to 160 °C to form a homogeneous solution. After cooling down to room temperature, 10 mL methanol solution containing NaOH and NH₄F was slowly added with stirring for 30 minutes. The solution was then heated to 300 °C for 1h under Argon protection and cooled down to room temperature. The NaYF₄: Yb, Er nanoparticles were precipitated with ethanol and washed with ethanol/water (1:1 v/v) for three times. These as-prepared nanoparticles were dispersed in cyclohexane, CO-520 and ammonia were then added to form a water-in-oil microemulsion. After sonicating for 20 min, TEOS was added into the microemulsion with stirring for two days, resulting in SiO₂-coated nanoparticles. They were precipitated by adding acetone and were washed with ethanol/water (1:1v/v) twice.

2.3.Preparation of Ag nanostructures on silica beads

The deposition of Ag nanostructures onto silica beads was performed using a protocol previously reported by our group [33]. Firstly, APTMS was added to the silica beads solution with stirring overnight. Secondly, the ~10 nm as-prepared Au colloids were added to the above solution with stirring for 30–90 min to allow them to bind to the silica surface, followed by washing with nanopure water 3 times. These Au colloids act as seeds for further deposition of Ag which surrounds and encapsulates each of the Au nanoparticles. The deposition of Ag nanostructures on the silica beads was carried out as follows: equal amounts of the silver enhancer solutions A and B were mixed using a vortex, followed by addition to the Au-silica solution with reaction for 3 min. This process was carried out in the dark as the silver enhancer kit is light-sensitive. The resulting Ag nanostructure-coated silica beads were centrifuged and washed with nanopure water 3 times to terminate the reaction between silica beads and the enhancer solution.

2.4.Conjugation of SA with SiO₂-coated NaYF₄: Yb, Er

5 µL of APTMS and 400 µL of ammonia (wt 30%) were added to 20 mL ethanol solution containing 1 mg of SiO₂-coated NaYF₄: Yb, Er nanoparticles. After stirring for 24 hrs at room temperature (R. T.), nanoparticles were centrifuged and washed twice with ethanol and 3 times with nanopure water to completely remove unreacted materials. These nanoparticles were then added to 2 mL of PBS buffer containing 0.5 mg SA and 0.3mL of 1% glutaraldehyde (see Fig. 1a). After stirring again for 22 hrs at 4 °C, 1.0 mg of NaBH₄ was added and the solution was incubated for 2 hr at R. T. The nanoparticles were centrifuged and washed with PBS buffer 3 times. The SA-UC nanoparticle conjugates were stored at 4 °C before use.

2.5. SA-biotin-based assay

The glass slides were cleaned by soaking in the piranha solution overnight and then rinsed with nanopure water and dried in air before use. The slides were then dip coated with poly-L-lysine solution (freshly prepared solution: 8 mL of water + 1.0 mL of 1% poly-L-lysine solution + 1.0 mL of PBS buffer, pH 7.4). After drying in air, each slide was covered with tape containing punched holes to form wells on the surface. Each well was filled with a 20 µL suspension of silica beads: the first slide with Ag-coated silica beads and the second with uncoated silica beads. After drying in air, each well was filled with 20 µL of 40 µg/mL biotinylated rabbit anti-mouse IgG antibody solution. The slides were incubated overnight in a humid chamber and rinsed with PBST (PBS with 0.05 % Tween 20) and PBS, which were

used in all washing procedures. Blocking was performed by adding the BSA solution and incubation for 1 hour in a humid chamber to minimize non specific binding. After rinsing, each well was incubated for 1 h with 20 μ L per well of SA-UC nanoparticle conjugates, followed by a rinse and stored at 4°C before measurement (see Fig. 1b).

2.6.Preparation of gold shell-coated NaYF₄: Yb, Er nanoparticles (second experimental system)

Synthesis of the gold shell-coated nanoparticles was implemented by employing a facile one-pot technique [30]. Briefly, 0.2 M solution of YCl₃, YbCl₃ and ErCl₃ comprising 78% YCl₃, 20% YbCl₃ and 2% ErCl₃ was mixed with 0.2 M sodium citrate and 1 M NaF solution in a 1: 2: 4 volume ratio and heated to 90 °C. Then 380 nanomoles of 0.1% HAuCl₄ were added to the formed solution, with heating continued for two and half hours. The pink colored nanoparticles were centrifuged which causes them to precipitate as solids and dried at 80–100 °C. The resulting product in form of a solid crust several mm thick was crushed to form a mixture of micro- and original nanoparticles and heated to 450 °C for 12 h in a N₂ flow furnace, followed by suspension in water.

2.7.Characterization

The extinction spectra of silica beads with and without Ag nanostructures were measured using a Cary spectrophotometer (Cary 5000 UV-vis-NIR, Varian Inc.). Transmission electron microscopy (TEM) images were taken on a PHILIPS CM10 system at an accelerating voltage of 100 kV. The samples were prepared by placing a drop of dilute ethanol dispersion containing samples on the surface of a copper grid. UC luminescence spectra were obtained using a Fluorolog-Tau-3 system (JY Horiba). In this measurement, the glass slides with dry samples were maintained at a 45° illumination in an upright position in the solid sample holder. The spectral width was set to 8 nm. The emission spectrum was recorded over a range of 500–750 nm. UC luminescence lifetime was measured using purpose-built epi-fluorescence microscopy system ($\times 10$ objective; dichroic beam splitter (Zeiss, FT395)). In the measurements, a pair of emission filters (FF01-543/22-25 BP Filter from Semrock (543 nm, 25 nm bandpass) for green emission and 5915-A clarity BP filter (640nm, 30nm bandpass) from Newfocus for red emission) were employed to extract green and red emission, respectively. A diode laser (980 nm, maximum 1 Watt in CW mode) (Beijing Viasho Technology Co., Ltd), with a 1 m fiber (N.A: 0.22 and $\varnothing$ 200 μ m core) were used as the excitation source in both UC spectrum and lifetime measurements. We used 500 μ s pulses at 1 kHz triggered by TTL signals. The UC signal was collected by a cooled (–20 °C) SPMMini3035X08A1 solid-state photomultiplier (SPMT) from SensL. The preamplifier electronics was configured to have a bandwidth of 2 MHz. The system was able to detect signals with decay times longer than 150 ns. The samples were measured dry. The values of lifetime were derived by a single exponential curve fitting (Origin 8.0 software) with the residual error function χ^2 value of less than 1.0.

3. Results and discussion

The surface modification of these nanoparticles in the first experimental system was achieved using a silica coating which protects the core from the environment and can be modified with amines, thiols and carboxyl groups. The uniformity of pure and silica-coated nanoparticles was confirmed by TEM images (Fig. 2a, c, d). The average size of nanoparticles was ~28 nm and the thickness of the silica shell was ~11 nm. The corresponding UC luminescence spectrum exhibits three distinct Er³⁺ emission bands around 525nm, 545 nm and 660 nm which correspond to ²H_{11/2} → ⁴I_{15/2}, ⁴S_{3/2} → ⁴I_{15/2} and ⁴F_{9/2} → ⁴I_{15/2} transitions, respectively (Fig. 2b) [34]. In the second system, the presence of gold shells was confirmed by the TEM image, as shown in Figure 3a. The TEM studies

also confirmed that Au coating had good uniformity and reproducibility. Figure 3b shows the absorption spectra of Au coated and uncoated samples, where coated nanoparticles display a green plasmon band around 510–560 nm. The respective size histograms are presented in Figure 3c.

The TEM images and extinction spectra of Ag nanostructure-coated silica beads were obtained to verify the size and surface plasmon energy (Fig. 4). Fig. 4a shows the TEM image of Ag nanostructure-coated silica beads. As expected, Au nanoparticles on silica beads served as nucleation sites for growth of silver nanostructures, producing controlled, high and relatively even silver coverage. The formation of silver nanostructure clusters was also observed. In such clusters, where particles are in close proximity, the coupling of the neighbouring particles plays an important role and modifies the dipole-dipole interaction between the dipole moments of the coupled particles. This dipole coupling concept has been successfully applied to the modeling of the optical properties of the silver fractal clusters [35]. Fig. 4b shows the corresponding extinction spectra of silica beads with and without Ag nanostructures. The obvious Ag plasmon peak at around ~400 nm was observed with Ag nanostructures adhering to the silica surface compared to that from pure silica beads. Moreover, the shape of such extinction spectra suggests that light incident on the silica beads is scattered by silver nanostructures.

We first assessed the effect of silver nanostructures on UC luminescence amplification using SA-biotin binding system. The glass slide was coated with Ag-silica beads and biotinylated IgG antibody molecules; SA-UC nanoparticle conjugates were then bound to silica beads via the avidin-biotin recognition mechanism. The impact of the nearby Ag nanostructures on luminescence was measured. We checked the effect of these nanostructures on the spectral shape of the UC emission. In the samples with and without Ag nanostructures as shown in Figure 5a, we were able to observe very similar spectral signatures, with the emission bands typical of Er^{3+} around 525 nm, 545 nm and 660 nm. Ag nanostructures clearly enhanced UC luminescence with enhancement factors of ~4.4 and ~3.5 for green and red emission, respectively, compared to those from the control sample without Ag nanostructures. These values were obtained by dividing the integrated luminescence intensities for samples with Ag nanostructures after background subtraction (integrated luminescence intensities around 525 nm, 545 nm and 660 nm wavelengths only, from Ag nanostructures without the bioassay) by those without Ag nanostructures. The intensity values were also corrected for the differences in the number of nanoparticles bound in each sample, determined from the Er fluorescence of the top solution remaining after the completion of bioassays. For a more complete characterization of the effect of Ag nanostructures on UC luminescence we also carried out lifetime measurements. As discussed in the literature, MEF is characterized by an increase in the quantum yield and a decrease in the lifetime of a fluorophore located in the proximity of a metallic nanostructure [36]. The fluorescence lifetime provides unambiguous confirmation of the metal-induced fluorescence enhancement effect in the first system. The measured decay curves of UC luminescence from samples with and without Ag nanostructures indicate a clearly decreased lifetime observed in the presence of the silver nanostructures near these nanoparticles (Fig. 6), which was reduced from 211 μs to 127 μs for green emission and from 654 μs to 276 μs for red emission, respectively. Such reduced lifetime has two major implications, higher photostability and a higher number of emitted photons per unit time under the same excitation conditions. Both these properties make it possible to use shorter exposure time or obtain higher signal to noise for comparable exposure times, thus increasing sensitivity and detectivity in luminescence measurements.

In general, MEF arises from the enhancement of the local electromagnetic field (referred as excitation enhancement) and also from an increase in the radiative decay rate (referred as emission enhancement). The distinction between these two contributions is usually not

simple but an estimate of relative contributions is possible from the data in Figures 5a and 6. Excitation enhancement produces a higher excitation rate but it does not change the lifetime of the fluorophore. When the interparticle distances are reduced, the enhancement of the local electromagnetic fields becomes strong [36], which magnifies the excitation enhancement induced by these nanostructures. In our case, the silver nanostructures on the surface of the silica beads were very close to each other, resulting in strong coupling effect between nanostructures. This coupling effect has a significant effect on the exciting electromagnetic field [24–25, 37]. We also found that the enhancement was not equal for both emission bands. The luminescence enhancement for the green band was higher compared to the red band because the Ag plasmon had a better overlap. This wavelength-dependent enhancement can be attributed to emission enhancement [27]. Therefore, both excitation and emission enhancement are likely to have contributed to the strong UC luminescence enhancement in this case. In addition, the luminescence decays of samples with Ag nanostructures were shorter than those of the control samples without Ag nanostructures, which is in accordance with previously described MEF [24–25, 27, 38]. This provides additional evidence for the partial contribution from emission enhancement, which can also reduce the lifetime of the fluorophores [36].

We extended a similar analysis to the second system under investigation, the gold shell-coated nanoparticles. As shown in Figure 5b, in samples with gold nanoshells both green and red emissions were increased, by a factor of ~9.1 times and ~6.7 times, respectively. Investigations on metal surface enhanced luminescence of nanocrystals indicate that the degree of fluorescence enhancement is correlated with the spectral overlap between the absorption or emission band of the phosphors and the surface plasmon band of metals [39]. Therefore one could attribute this larger enhancement (~9.1-fold) for green emission to better spectral overlap of the gold plasmon band between 500–550 nm with the green luminescence, which can cause a better plasmonic coupling. We also found that the enhancement value (~6.7-fold) for red emission induced by gold nanoshells was higher, compared to that induced by silver nanostructures (~3.5 fold), and this again would be consistent with the same argument. However other effects can also produce similar relationships between fluorescence intensities. The ratio of red to green upconversion fluorescence depends on nanoparticle size, and therefore it may not be the same for the Ag-enhanced and Au-coated nanoparticles whose NaYF₄ core sizes are not identical. The fluorescence enhancement depends on the proximity of the fluorophore to the metal, and, for the Ag nanoparticles, it depends on the length of the molecular linker; this distance for Ag and Au structures is different. Hence the relationship between the red and green fluorescence intensity in case of each metal (Ag and Au) or between Ag and Au nanostructures for selected (red or green) intensities can not provide unequivocal support that the fluorescence enhancement in Au-coated samples is due to plasmonic effects. In contrast, the upconversion lifetimes in Au-coated nanoparticles very clearly show the behaviour opposite to that expected in the case of metal enhancement acting in isolation. Figure 7 shows that the red emission in gold shell-coated samples had a longer lifetime (~1190 μ s) than in uncoated ones (~812 μ s), while the lifetimes of the green emission in these two samples are similar (~882 μ s). These lifetime values can be interpreted when we consider the effect of surface recombination which is known to affect the green/red upconversion in a major way [40–41]. This surface recombination may be different in gold-shell coated and uncoated nanoparticles. Its effect is superimposed and may dominate over the plasmonic effects. The plasmonic effect of the gold shell coating is expected to reduce the lifetime in both green and red band, while the same coating may protect nanoparticles from surface recombination, producing the opposite effect of extending the lifetimes. Thus we interpret the similarity of lifetimes in Au-coated nanoparticles and uncoated nanoparticles as due to surface recombination counterbalancing the plasmonic effects.

Finally we discuss how the presence of quite significant fluorescence enhancement in Au-coated samples can be reconciled with comparatively similar upconversion fluorescence lifetimes for Au-coated and uncoated samples. This fluorescence enhancement can be caused by the fact that the Au-coated nanoparticles experience different and higher electric field under the same excitation conditions as the uncoated samples, which means excitation enhancement is in operation. Such enhanced electric field due to the presence of metal nanoshells has been extensively discussed in Ref [42].

4. Conclusion

We demonstrated the feasibility of using both silver nanostructures and gold nanoshells for UC luminescence enhancement. These two types of noble metal nanomaterials produced clear luminescence enhancement (~4.4-fold for green emission and ~3.5-fold for red emission in the case of silver nanostructures; ~9.1-fold and ~6.7-fold in the case of gold nanoshells). We also demonstrated reduced luminescence lifetimes induced by Ag nanostructures, confirming the MEF effect applied to UC luminescence enhancement. The lifetime results for gold nanoshells (extension of red lifetime and no change of green lifetime upon Au coating) are attributed to a combination of plasmonic and surface recombination effects which can not be untangled in this geometry. Although further study will be necessary to fully elucidate the exact underlying mechanism, our results prove that UC emission can be enhanced by noble metals such as silver and gold, which promise to yields a broader range of applications of metal-UC nanoparticle composites in bioassays, bioimaging, and energy conversion that require ultrahigh sensitivity and low background.

Acknowledgments

The project described was supported in part by Award Number P42ES004699 from the National Institute of Environmental Health Sciences. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institute of Environmental Health Sciences or the National Institutes of Health. The support of USDA Award number 2009-35603-05070 is also gratefully acknowledged.

References

1. Hu H, Xiong L, Zhou J, Li F, Cao T, Huang C. Chem. Eur. J. 2009; 15:3577–3584. [PubMed: 19219877]
2. Kumar R, Nyk M, Ohulchanskyy TY, Flask CA, Prasad PN. Adv. Funct. Mater. 2009; 19:853–859.
3. Nyk M, Kumar R, Ohulchanskyy TY, Bergey EJ, Prasad PN. Nano Lett. 2008; 8:3834–3838. [PubMed: 18928324]
4. Yu M, Li F, Chen Z, Hu H, Zhan C, Yang H, Huang C. Anal. Chem. 2009; 81:930–935. [PubMed: 19125565]
5. Feng J, Shan GM, Maquieira A, Koivunen ME, Guo B, Hammock BD, Kennedy IM. Anal. Chem. 2003; 75:5282–5286.
6. Qin X, Ju YG, Bernhard S, Yao N. J. Mater. Res. 2005; 20:2960–2968.
7. Weiss S. Science. 1999; 283:1676–1683. [PubMed: 10073925]
8. Seifert JL, Connor RE, Kushon SA, Wang M, Armitage BA. J. Am. Chem. Soc. 1999; 121:2987–2995.
9. Alivisatos AP, Gu W, Larabell C. Annu Rev Biomed Eng. 2005; 7:55–76. [PubMed: 16004566]
10. Michalet X, Pinaud FF, Bentolila LA, Tsay JM, Doose S, Li JJ, Sundaresan G, Wu AM, Gambhir SS, Weiss S. Science. 2005; 307:538–544. [PubMed: 15681376]
11. Wang F, Liu X. J. Am. Chem. Soc. 2008; 130:5642–5643. [PubMed: 18393419]
12. Stolik S, Delgado JA, Pérez A, Anasagasti L. J Photoch Photobio B. 2000; 57:90–93.
13. Mader HS, Kele P, Saleh SM, Wolfbeis OS. Current Opinion in Chemical Biology. 2010; 14:582–596. [PubMed: 20829098]

14. Auzel F. Chem Rev. 2004; 104:139–173. [PubMed: 14719973]
15. Wang F, Liu X. Chem Soc Rev. 2009; 38:976–989. [PubMed: 19421576]
16. Lakowicz J. Anal. Biochem. 2005; 337:171–194. [PubMed: 15691498]
17. Lakowicz JR, Shen Y, D'Auria S, Malicka J, Fang J, Gryczynski Z, Gryczynski I. Anal. Biochem. 2002; 301:261–277. [PubMed: 11814297]
18. Sokolov K, Chumanov G, Cotton T. Anal. Chem. 1998; 70:3898–3905. [PubMed: 9751028]
19. Geddes CD, Cao H, Gryczynski I, Gryczynski Z, Fang J, Lakowicz JR. J. Phys. Chem. A. 2003; 107:3443–3449.
20. Malicka J, Gryczynski I, Geddes CD, Lakowicz JR. J. Biomed. Opt. 2003; 8:472–478. [PubMed: 12880353]
21. Lakowicz JR, Malicka J, Gryczynski I. Biotechniques. 2003; 34:62–68. [PubMed: 12545541]
22. Sun YY, Jiu HF, Zhang DG, Gao HG, Guo B, Zhang QJ. Chem. Phys. Lett. 2005; 410:204–206.
23. Zhang J, Fu Y, Lakowicz JR. J. Phys. Chem. C. 2009; 113:19404–19410.
24. Jin YD, Gao XH. Nature Nanotechnology. 2009; 4:571–576.
25. Ray K, Badugu R, Lakowicz JR. J. Am. Chem. Soc. 2006; 128:8998–8999. [PubMed: 16834349]
26. Link S, El-Sayed MA. J. Phys. Chem. B. 1999; 103:8410–8426.
27. Mertens H, Polman A. Appl. Phys. Lett. 2006; 89:211107.
28. Karmakar B, Som T. J. Appl. Phys. 2009; 105 013102.
29. Aisaka T, Fujii M, Hayashi S. Appl. Phys. Lett. 2008; 92:132105.
30. Sudheendra L, Han J-H, Kennedy IM. Proc. of SPIE. 2010; 7576:75760Y–75765Y.
31. Zhang J, Badugu R, Lakowicz JR. Plasmonics. 2008; 3:3–11. [PubMed: 19890452]
32. Li ZQ, Zhang Y, Jiang S. Adv. Mater. 2008; 20:4765–4769.
33. Deng W, Drozdowicz-Tomsia K, Jin D, Goldys E. Anal. Chem. 2009; 81:7248–7255. [PubMed: 19715357]
34. Boyer J-C, Vetrone F, Cuccia LA, Capobianco JA. J. Am. Chem. Soc. 2006; 128:7444–7445. [PubMed: 16756290]
35. Karpov, SV.; Bas'ko, AL.; Popov, AK.; Slabko, VV.; George, TF. Research Signpost. Vol. 2. Trivandrum, India: 2002. p. 427-463.
36. Li K, Stockman MI, Bergman DJ. Phys. Rev. B. 2005; 72:153401–153405.
37. Liu N, Prall BS, Klimov V. J. Am. Chem. Soc. 2006; 128:15362–15363. [PubMed: 17131988]
38. Geddes CD, Lakowicz JR. J. Fluoresc. 2002; 12:121–129.
39. Chen Y, Munechika I, Plante JL, Munro AM, Skrabalak SE, Xia Y, Ginger DS. Appl. Phys. Lett. 2008; 93 053106.
40. Lü Q, Guo F, Sun L, Li A, Zhao L. J. Phys. Chem. C. 2008; 112:2836–2844.
41. Wang F, Wang J, Liu X. Angew. Chem. Int. Ed. 2010; 49:7456–7460.
42. Wu D, Xu X, Liu X. Sol. St. Commun. 2008; 148:163–167.

Figure 1.
Schematic representation of conjugation SiO₂-coated nanoparticles with streptavidin (SA)
(a) and a SA-biotin-based assay (b).

Figure 2.

TEM image of SiO₂-coated NaYF₄: Er, Yb (a), the UC luminescence spectra of SiO₂-coated NaYF₄: Er, Yb nanoparticles (b), histograms of shell thickness (c) and core diameter (d).

Figure 3.

TEM image of gold shell-coated NaYF₄: Er,Yb nanocrystals (a), absorption spectra of Au coated and uncoated nanoparticles (b) and size distribution of coated and uncoated nanoparticles measured by dynamic light scattering (c).

Figure 4. TEM image of Ag nanostructure-coated silica beads (a) and absorption spectra of the pure and Ag nanostructure-coated silica beads (b)

Figure 5.
The UC luminescence spectra observed from NaYF₄: Er, Yb nanoparticles with and without Ag nanostructures (a) and with and without gold nanoshells (b).

Figure 6. Representative UC luminescence decay times of green (a) and red (b) emissions from $\text{NaYF}_4\text{: Er,Yb}$ nanoparticles with and without Ag nanostructures.

Figure 7. Representative UC luminescence decay times of green (a) and red (b) emissions from NaYF_4 : Er,Yb nanoparticles with and without gold nanoshells.