Tuning sputtered gold thickness to enhance absorption and emission in core-shell type erbium doped upconversion nanoparticles

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Abstract. Upconversion nanoparticles (UCNPs) converts near-infrared excitation to visible emission with advantages e.g. photostable, non-blinking, and background-free probes for bioimaging and biosensor. However, low quantum yield and low efficiency (~1%) as drawback need to be enhanced. A plasmonic gold nano-structured surface was designed and fabricated to couple with the 980 nm radiation and produce plasmonic enhancement of the upconversion luminescence. The synthesis of the UCNPs was done by thermal decomposition and SiO2 coating prepared by the reverse microemulsion process. Here, we report a novel tunable plasmon-enhanced fluorescence by modulating the thickness and surface roughness of gold island film on Si. The localized surface plasmon resonance (LSPR) at 980 nm was obtained, matched with the native excitation of UCNP results in maximum enhancement of 10-fold of green emission band at 540 nm for the Er-doped UCNPs.

1. Introduction
Lanthanide-doped upconversion nanoparticles (UCNPs) can use infra-red (IR) excitation for its visible emission, which is fit for deep tissue imaging [1]. The upconversion process employs sequential absorption process of multiple low energy (IR) photons, the use of long lifetime, and through ladder-like energy levels of trivalent lanthanide ions embedded in a suitable inorganic host lattice to produce higher energy (visible) anti-Stokes luminescence [1]. Nevertheless, the major drawback of UCNPs is low (<1%) quantum yield due to the small absorption cross-sections. The low quantum yield/efficiency in these UCNPs can be enhanced by different techniques, and among various strategies metal-enhanced fluorescence (MEF) is a focus in this study. Normally, adjacent metallic structures quench fluorescence from fluorophores [2]. However, if placed at a certain distance away from them, these metallic structures can enhance fluorescence. In this paper, we have adopted the plasmonic enhancement technique for the luminescence enhancement. A novel sputtered gold substrate has been used whose preparation is experimentally simple. We have used a silica spacer on the lanthanide doped UCNPs to create the separation [3], and dispersed these particles on the gold-
coated substrate to optimize the plasmonic enhancement of the emission. The objective of enhancing the luminescence by surface plasmons in a gold film is schematically shown in figure 1.

2. Experimental

2.1. Materials
Ytterbium(III) chloride (YbCl₃, 99.99%), yttrium trichloride (YCl₃, 99.99%), erbium(III) chloride (ErCl₃, 99.99%), polyoxyethylene(5) nonylphenylether (IGEPAL CO-520), sodium hydroxide (NaOH, 98%), ammonium fluoride (NH₄F, 98%), silver nitrate (AgNO₃, 98%), ethylene glycol (99%), and ethanolamine (99%) were purchased from Sigma-Aldrich (USA). Oleic acid (90%), octadecene (90%), and tetraethyl orthosilicate (TEOS, >99%) were purchased from Acros (Belgium). All the chemicals were used as received from the vendors without any further purification.

2.2. Synthesis of NaYF₄:Yb,Er core nanoparticles
Upconverting lanthanide NaYF₄:Yb,Er nanoparticles were synthesized as follows [4]: YCl₃ (0.8 mmol), YbCl₃ (0.18 mmol), and ErCl₃ (0.02 mmol) were mixed with 6 ml oleic acid and 15 ml octadecene in a 50 ml flask. The solution was heated to 160 °C under vigorous stirring to form a homogeneous solution and then cooled to room temperature. Subsequently, 10 ml methanol solution of NaOH (2.5 mmol) and NH₄F (4 mmol) were slowly added to the flask and vigorously stirred for 30 minutes. The solution was heated slowly to remove methanol, degassed at 100 °C for 10 minutes, followed by heating at 300 °C for 1 h under nitrogen flow. The solution was remained undisturbed and cooled naturally; afterwards, the nanoparticles were precipitated from the solution with acetone and washed with ethanol/water (1:1 v/v) for three times.

2.3. Synthesis of the SiO₂ shell as spacer on the NaYF₄:Yb,Er nanoparticles
The coating procedure of the NaYF₄:Yb,Er nanoparticles with a SiO₂ layer as a spacer was reported previously [4] as follows: 0.1 ml of CO-520, 6 ml of cyclohexane, and 4 ml of 10 mM NaYF₄:Yb,Er nanoparticles solution in cyclohexane were mixed and stirred for 10 minutes. 0.4 ml of CO-520 and 0.08 ml of 30 wt.% ammonia were then added to the mixture solution and the container was sealed and sonicated for 20 minutes until a transparent emulsion was formed. Subsequently, 0.04 ml of TEOS was added to the solution. The thickness of silica coated outside UCNPs could be adjusted by controlling the concentration of TEOS. The solution was stirred for 48 hours at a speed of 600 rpm. Finally, NaYF₄:Yb,Er/SiO₂ core/shell nanoparticles were precipitated by adding acetone, and washed with ethanol/water (1:1 v/v) twice and re-dispersed in water.

Synthesis and preparation of gold nanostructured film layer on crystalline silicon (c-Si) substrates for MEF was done as follows: first, Si substrates (2 cm × 3 cm) were cleaned and sonicated in deionized water and acetone, separately, for 15 and 30 minutes, respectively, followed by drying under a nitrogen stream. Gold was coated on substrates by a sputter coater (Emitech K550X, United Kingdom) for 2, 4, and 8 minutes. Subsequently, 2 ml of 10 mM NaYF₄:Yb,Er/SiO₂ core/shell nanoparticles were dropped on each of gold coated c-Si substrates and dried in ambient air. The proposed schematic to study metal-enhanced fluorescence effect between UCNPs and different thickness of gold sputtered on a silicon substrate (2, 4, and 8 minutes) has shown in figure 1.

2.4. Characterization of morphology, structure, and emission
Transmission electron microscope (TEM) and scanning electron microscopy (SEM) imaging for morphology and surface roughness of gold thin film coated silicon wafer was performed using TEM JEM-2000EX (JEOL, Japan) and Field Emission SEM 6700F (JEOL, Japan), respectively. UV-Vis absorption measurement was performed using UV-Visible-Near Infrared spectrophotometer (V-770, JASCO, Japan). Upconversion and metal-enhanced fluorescence spectra were measured by Fluorolog-3 fluorescence spectrofluorometer (Jobin Yvon, USA) using 980 nm laser head (SDL-5000T, Shanghai, China) with 60° angle of incident and power up to 5 W as the excitation source.
3. Results and discussion

Figure 2a and b shows typical TEM images of the NaYF$_4$:Yb,Er core and core-shell upconversion nanoparticles. The core UCNPs have a lattice spacing of 0.3 nm, and diameter of 8±2 nm (figure 2a). The use of the dense SiO$_2$ coating on the core UCNP is important for stabilizing the core and enabling dispersion in aqueous media instead of cyclohexane which cannot be used for cellular or tissue imaging. Another reason to use the SiO$_2$ layer as a gap between UCNPs and metal structured for MEF. The core-shell UCNPs has shown in figure 2b and obtained 7 nm of silica thickness.

Figure 2c described energy transfer upconversion (ETU) mechanism. ETU is a process which employs two types of luminescent centers, which are usually called the sensitizer (Yb$^{3+}$) and activator (Er$^{3+}$), embedded in the crystal matrix. Under the excitation of photons with lower energy, both the sensitizer and the activator would be excited. With the non-radiative energy transfer from the sensitizer to the adjacent activator, sequential absorption of the activators to the higher excited state takes place. Radiative emission could be observed as the activator returned to the ground state. In Yb$^{3+}$–Er$^{3+}$ dual ions activated systems, green emissions at 520 and 540 nm together with red emissions at 650 nm are frequently observed characteristics. Moreover, another peak, particularly in blue emission bands such as 380, 410, and 487 nm, also appeared in weak intensity (figure 2c).

Figure 2d exhibit the up-conversion emission spectra of the core (black line), and core-shell (red line) type nanoparticles under 2 W excitation. The fluorescence spectra indicated signal reduction up to 25% after SiO$_2$ coating has been applied on the surface of UCNPs core. Similarly, the optical photograph in the inset of figure 2d display the intensity of core-shell that was weaker than core, which indicates SiO$_2$ coating as a spacer for MEF purpose reduced the intensity of UCNPs.

Metallic (Au or Ag) nanostructures including nanofilms and nanoparticles have been widely used in metal-enhanced fluorescence including the UCNPs [5]. The optical properties of metal films can be tailored by manipulating the organization of the constituent nanostructures, columns [5, 6], islands, or layers. Specifically, ultrathin gold or silver island films shows frequency tunable surface plasmon (SP) absorption bands in the visible and near-infrared (400 – 1000 nm) [7, 8]. The localized surface plasmon resonance (LSPR) of the metallic nanostructures then increases the radiative rate and/or the excitation intensity producing the luminescence enhancement. The luminescence quenching that stems from resonance energy transfer from the fluorophore or UCNPs to the metallic structure can be prevented by introducing a spacer layer to delineate the fluorophore from the metal [9]. MEF in
UCNPs has been reported before by using a variety of gold or silver nano-morphologies including film [10], nanoparticles [11], and nanorods [12].

Figure 2. TEM image of NaYF₄:Yb,Er (a) core and (b) core-shell. The inset indicated high magnification TEM image of core and core-shell. (c) Upconversion mechanism of the Yb,Er. Under excitation at 980 nm, an electron of Yb³⁺ is excited from the ²F₇/₂ to the ²F₅/₂ level. The energy may be transferred to Er³⁺ non-radiatively to excite it to the corresponding excited level. For Yb,Er co-doped UCNPs, the emission bands at 520, 540, and 650 nm assigned to ⁴H₁₁/₂ - ⁴I₁₅/₂, ⁴S₃/₂ - ⁴I₁₅/₂, and ⁴F₉/₂ - ⁴I₁₅/₂ transitions of Er³⁺. (d) The up-conversion emission spectra of the core (black line), and core-shell (red line) type nanoparticles under 2 W excitation. The inset shows an optical photograph of the tube showing green luminescence from core (NaYF₄:Yb,Er) and core-shell (NaYF₄:Yb,Er/SiO₂).

In this paper, we introduce our design of thin film metallic nanostructures for the observation of MEF in the UCNPs (figure 1). The gold layer would be tunable in surface coverage, morphology, and thickness by adjusting the sputtering time. With a sputtering machine at our disposal this would mean low density gold nano-islands, coalesced gold islands, and thick layers of a gold island with gold nano-clusters, with increasing sputtering time. Fixed volume core-shell structure (NaYF₄:Yb,Er/SiO₂) UCNPs dispersed on clean silicon served as the control and gold coated silicon with different time deposition (figure 1). Gold-coated silicon was optimized for the maximum luminescence from the same volume of UCNPs dispersed on them. We have carefully prepared gold-coated silicon substrates by sputtering and optimized for the best MEF.

Figure 3 shows the SEM and AFM images of the gold layer on c-Si, displaying morphology for sputtering times of 2, 4, and 8 minutes. The SEM images clearly reveal discontinuous gold island film.
morphology for 2 minutes coating time (figure 3a), which becomes a coalesced quasi-continuous film by 4 minutes (figure 3b) coating time. Further increase in the sputtering time yielded fully coalesced, continuous, and comparatively thicker gold films (figure 3c). Figure 3e – g shows a representative AFM image of the gold nanostructure for different sputtering times. The surface roughness of the gold nanostructures for 8 minutes sputtering time, as shown in figure 3g, is higher than 2 and 4 minutes and the data has been consistent with the SEM images. Coupling of the UCNPs with these metallic surfaces should lead to enhanced fluorescence going by earlier reports [9, 13]. Tuning the optical reflection of the gold nanostructures may efficiently couple more light into, and concentrate plasmonic electric field at the UCNP site to facilitate enhanced fluorescence.

![Figure 3](image)

**Figure 3.** Top view SEM and AFM images showing the morphology of the gold island films on Si substrate produced by sputtering for (a, e) 2, (b, f) 4, and (c, g) 8 minutes, respectively. (d) Reflectance spectra of silicon only (star), and silicon substrates coated with 2 (triangle), 4 (circle), and 8 (square) minutes of gold by sputtering. Short dash line shows NaYF₄:Yb,Er/SiO₂ absorption band at 980 nm.

To verify our hypothesis mentioned above, fixed volume of UCNPs were dispersed on these gold coated c-Si and measured for their luminescence. To characterize the gold nanostructures, number identification tags would be used to represent sputtering time (in minutes) of gold coating. Therefore, (0) would represent luminescence from UCNPs on bare c-Si or control, (2) would represent a sample with a bottom gold layer of 2 minutes, and (8) would imply a gold thin film layer of 8 minutes. All samples were prepared and measured under identical conditions.

Figure 4a exhibits MEF from the core-shell UCNPs for samples (2), (4), and (8) compared to (control), where (8) showed the best fluorescence signal which we would identify as the optimized bottom gold layer coating time. Maximum enhancements of ~8, ~9, and ~10 fold were observed for the 520, 540, and 650 nm emissions, respectively, for the (8) compared to the (control) configuration. The spectral emissions were similar to those in solution (figure 4b) with signature peaks at 540 and 650 nm, and a comparatively weaker emission peak at 520 nm. The intensity variation of the main spectral features of the UCNCP emission at 520, 540, and 650 nm, as a function of excitation power density, is shown in figure 4b – d, respectively, for all configuration. The slopes of the linear fits of the intensity variation (figure 4b – d) are between 2.6 – 3, signifying approximately 2 – 3 participating photons (n) in the luminescence process which is consistent with earlier reports [14]. This presentation would reflect the efficacy of the bottom gold layer, in the emission process with respect to those without any use of gold. The gold thin film nanostructures (8) yields an enhancement factors of ~ 8, 9, and 10 for the emissions at 520, 540, and 650 nm, respectively, against the no-gold (control) configuration. The 8 minutes gold sputtered on c-Si proved to be the most efficient enhancer of luminescence compared to other configurations.

To understand the effect of the gold nanostructured layer, we have to study their optical properties by considering the reflectance spectra of a gold nanostructured layer on silicon as shown in figure 3d. The bare Si substrate, as control, shows typical silicon reflectance spectra with a decreased absorption
below the band gap 1100 nm energy. The data shows that the reflectance near 980 nm increase significantly (absorption decreasing) with increasing thickness (2 – 8 minutes of sputtering) of the gold layer. The result indicates a mirror-like gold coating (8 minutes gold sputtering on Si) which reflects 90% of the 980 nm excitation which is also the absorption band of the UCNPs (shown by the dashed band around 1000 nm). The elevated reflection of the 980 nm radiation by the gold nanostructured layer would ensure increased optical path length and superior absorption in the UCNP layer. The enhancement was also observed on the 2 and 4 minutes gold coated Si substrates but in lesser proportions (figure 3d). The efficiency of MEF will be weaker on the discontinuous island films, as shown on 2 or 4 minutes gold coated Si substrates case, because a significant number of the UCNPs would be sitting on bare Si surface which would absorb instead of reflecting most of the available 980 nm radiation. The observed enhancement for the 2 and 4 cases, is similar to the one reported by Zhang et al [10] who obtained 5-fold enhancement just by a single coating the core UCNPs without a SiO$_2$ shell on them with gold NPs.

Figure 4. (a) Upconversion luminescence spectra, and power dependence of the (b) 520, (c) 540, and (d) 650 nm peak emission of NaYF$_4$:Yb,Er/SiO$_2$ on Si only (control), and Si coated with 2 (2), 4 (4), and 8 (8) minutes of gold. Laser power of 2 W was used in (a). The line joining the data points in (b – d) represents linear fits to the data points (symbols). The spectra in (a), and the symbols in (b – d) represent average measurements done on five different spots on the samples.

4. Conclusion
In summary, we have proposed and successfully demonstrated the use of a gold nanostructured layer for metal-enhanced fluorescence from NaYF$_4$:Yb,Er/SiO$_2$ core-shell nanoparticles (in solid state) with core sizes 8 nm in diameter prepared by thermal decomposition and ~7 nm thick SiO$_2$ shell prepared...
by the microemulsion technique. We have optimized a thick gold layer, with higher reflectance in the infrared region, to work best for the fluorescence enhancement by increasing the optical path length and therefore efficient multiphoton absorption of the excitation in the UCNPs layer. A maximum enhancement factor of 10 was observed when using the gold nanostructured layer compared to the bare nanocrystals without the use of any gold surface.

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References
[1] Kumar R, Nyk M, Ohulchansky T Y, Flask C A and Prasad P N 2009 Adv. Funct. Mater. 19 853
[2] Luther J M, Jain P K, Ewers T and Alivisatos A P 2011 Nat. Mater. 10 361
[3] Li Z, Zhang Y and Jiang S 2008 Adv. Mater. 20 4765
[4] Manurung R V, Wu C T, Roy P K and Chattopadhyay S 2016 RSC. Adv. 6 87088
[5] Jensen T R, Schatz G C and Van Duyne R P 1999 J. Phys. Chem. B 103 2394
[6] Yang B, Lu N, Qi D, Ma R, Wu Q, Hao J, Liu X, Mu Y, Reboud V, Kehagias N, Torres C M, Boey F Y, Chen X and Chi L 2010 Small 6 1038
[7] Shumaker-Parry J S, Rochholz H and Kreiter M 2005 Adv. Mater. 17 2131
[8] Myroshnychenko V, Rodríguez-Fernández J, Pastoriza-Santos I, Funston A M, Novo C, Mulvaney P, Liz-Marzán L M and García de Abajo F J 2008 Chem. Soc. Rev. 37 1792
[9] Lakowicz J R 2001 Anal. Biochem. 298 1
[10] Zhang H, Xu D, Huang Y and Duan X F 2011 Chem. Commun. (Camb.) 47 979
[11] Saboktakin M, Ye X C, Oh S J, Hong S H, Fafarman A T, Chettiar U K, Engheta N, Murray C B and Kagan C R 2012 ACS Nano 6 8758
[12] Feng A L, You M L, Tian L, Singamaneni S, Liu M, Duan Z, Lu T J, Xu F and Lin M 2015 Sci. Rep. 5 7779
[13] Schietinger S, Aichele T, Wang H Q, Nann T and Benson O 2010 Nano Lett. 10 134
[14] Pollnau M, Gamelin D R, Lüthi S R, Güdel H U and Hehlen M P 2000 Phys. Rev. B 61 3337