



Cavity controlled upconversion luminescence in Ag-capped NaYF₄:Yb,Er micron rod

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ABSTRACT

Ag-capped β -NaYF₄:Yb,Er micron rods were designed and fabricated to enhance their upconversion luminescence (UCL), which is in strong demand for various practical applications. Micro-spectral measurement was used to characterize the UCL of single rods. UCL of the Ag-capped β -NaYF₄:Yb,Er micron rods is enhanced by 4-fold compared to that of bare rods on glass, based on statistics from 32 rods, while UCL of rods on Ag film is only enhanced by 0.8-fold. Combination with back scattering spectra of several typical Ag-capped micron rods lead us to conclude that the stronger tailoring effect on UCL of Ag-capped rods can be explained by the stronger resonance confinement of light in the Ag-capped micron-rod cavities. UCL enhancement and strong fluctuations both in intensity and intensity ratio can be ascribed to modulation of radiative transition rates in different degrees, caused by variation of photonic mode densities around the emission wavelengths in various cavities.

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1. Introduction

Lanthanide-ion (Ln³⁺)-doped upconversion (UC) materials are able to convert near-infrared light into visible light efficiently, utilizing long-lived and ladder-like manifolds of Ln³⁺, mostly via sequential energy transfer processes [1,2]. Besides UC nano-materials are attractive due to their potential applications in life science and biomedicine [3–6], UC micron-materials are useful in lighting [7], display [8], and photovoltaic cells [9]. Unfortunately, the efficiency of UC luminescence (UCL) from Ln³⁺-activated materials is usually too low for viable implementation [10], determined by its nonlinear and forced electric-dipole transition properties. Therefore, methods for enhancement of their UCL are in strong demand.

UCL can be enhanced either via passive suppression of non-radiative decay or via active magnification of radiative transition. Suppression of non-radiative decay is the most popular method for nano-materials with large specific surface area [11,12], even up to two orders of magnitude enhancement has been reported [13], but is not working well to micron materials. Maybe magnification of radiative transition is a wise choose to enhance UCL of micron materials [14–16]. Although the probability of spontaneous emission is usually considered to be a constant, it is only valid when active ions located in a free space. It will be modulated when coupling to a local environment via change of photonic mode

density (PMD) according to Fermi's golden rule as $A_{ij} \propto |M_{ij}|^2 \rho(\nu_{ij})$ [17], where A_{ij} , M_{ij} , and $\rho(\nu_{ij})$ are the transition rate, the transition matrix element, and the density of the optical field (namely PMD) at the transition frequency between the excited state i and lower-energy state j , respectively. This method would be suitable for Ln³⁺ due to its very low intrinsic quantum efficiency [18]. The PMD can be increased via noble metal interfaces [19], photonic crystals [20], and resonant cavities [21,22]. Effective improvement of the PMD via metal interface usually locates in a very small volume [19], and the total effect will be tempered by averaging over the whole micron material. Photonic crystal with periodic structure is usually large in volume and complicated in fabrication [20], so is not suitable for miniaturization and mass-production. Building micron cavities based on randomly dispersed single UC particle or rod is a technically more feasible way to improve the PMD and then to enhance their UCL [15,16].

In this work, micron-scale UC rods are chosen to fabricate Ag-capped micron cavities, by coating the sparsely dispersed micron rods on glass slide with a thick Ag layer and then peeling off. UCL from single NaYF₄:Yb,Er micron rods with different sizes on glass slide, on Ag film, and in Ag micron cavities are studied via a microscope-based micro-spectroscopy system, which is a powerful technical approach to exploit microstructural dependent spectroscopic characters [23]. Statistical results show that UCL from Ag-capped rods is enhanced by 4-fold compared to bare rods on glass. Combination with corresponding back scattering spectra, the enhancement of UCL can be ascribed to the resonances around emission wavelengths in some cavities.

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2. Experimental and numerical simulations

β -NaYF₄:Yb,Er micron rods with length of $\sim 8 \pm 2 \mu\text{m}$ and diameter of $\sim 1.8 \pm 0.2 \mu\text{m}$ were synthesized using a hydrothermal route with similar procedure in literature [24]. Typically, 3.5 mL of aqueous solution containing 0.6 mmol of YCl₃, 0.135 mmol of YbCl₃, and 0.015 mmol of ErCl₃ was added into 7.5 mL of 30 °C aqueous solution containing 0.75 mmol of trisodium citrate under magnetic stirring. After vigorous stirring for 30 min, 4.7 mL of NH₄F aqueous solution (1 M) was dropped. After stirring for 15 min, the pH of the mixture was adjusted to ~ 5 by adding diluted HCl (1 M). After additional stirring for 45 min, the whole solution was transferred into a 25-mL PPL-lined stainless autoclave. Then the autoclave was sealed and kept in a baking oven at 180 °C for 24 h. As the autoclave was cooled to room temperature naturally in air, the precipitates were collected by centrifugation (1500 rpm, 5 min), washed with deionized water and ethanol in sequence. The final precipitates were dispersed in 4 mL deionized water for later use. The morphology of UC micron rods was characterized after sparsely dispersing on glass slide by a Zeiss Sigma scanning electron microscope (SEM).

A procedure for the formation of Ag nano-caps on nano-particles reported in Ref. [15] was adopted to fabricate Ag-capped micron rods. The colloid of UC micron rods was firstly diluted with water and sparsely spin-coated on cleaned glass slides, as shown in Fig. 1(a) [labeled as “Ref-1”]. Then, 200-nm-thick Ag coating layers were thermally evaporated twice onto the sample (Ref-1) tiltly from opposite sides. The thickness of the deposited Ag film was obtained from *Alpha*-step profiler measurement of planar, blank dummy samples processed in the same batches of the samples with UC micron rods. To peel off Ag-capped rods from the substrate, a precured polydimethylsiloxane resin (PDMS) slab was stamped onto the substrate surface and quickly peeled off from the substrate as such, the PDMS slab containing embedded Ag-capped β -NaYF₄:Yb,Er micron rods was obtained [labeled as “Sample”, shown in Fig. 1(a)]. Additionally, another type of sample was also prepared by spin-coating the diluted colloid onto a glass slide deposited with 200-nm-thick Ag film for reference [labeled as “Ref-2” in Fig. 1(a)].

UCL and back scattering spectra of single UC micron rod were measured using a homebuilt micro-spectroscopy system as shown in Fig. 1(b). The system is based on a trinocular microscope (BA310Met-T, Motic), additional confocal illumination and confocal

collection were combined into an observation tube. For UCL, $\sim 975 \text{ nm}$ laser was introduced via an optical fiber and focused onto the UC micron rods using an objective lens (100 $\times$, NA=0.8), the excitation power density on rods is $\sim 500 \text{ W/cm}^2$. UCL in a region of $\sim 1 \mu\text{m}$ in diameter was collected by the same objective lens, split from the excitation beam by a dichroic mirror, before being coupled into another optical fiber. The other end of the fiber was then connected to the entrance slit of a spectrograph (Omni- $\lambda 5008i$, Zolix) and detected by a charge coupled device (iDus, 401A-BV, Andor). In measurement of the back scattering spectra, the same setup was used, except that the input is white light from a halogen lamp and focused onto the UC micron rods using an objective lens (50 $\times$, NA=0.55) with lower magnification. Scattered light in an estimated area of $\sim 2 \mu\text{m}$ in diameter was collected in this condition. And finally the signal was analyzed by a fiber optic spectrometer (AvaSpec-2048, Avantes).

The simulations were performed with a two-dimensional (2D) finite-difference time-domain (FDTD) method using commercial software (FDTD Solutions).

3. Results and discussion

Fig. 1(c) shows a typical SEM image of an as-prepared β -NaYF₄:Yb,Er micron rod, which has serrated ends; its flat and smooth hexagonal cross sections indicate good crystallinity of the micron rod. Fig. 1(d) shows a typical SEM image of an upside-down Ag-capped micron rod, the marked cross section of the Ag layer outside lateral facet of rod implies the formation of Ag cap covering three facets of the hexagonally-shaped rod. Referring to the microscope image in Fig. 1(e), individual rods can be located and identified under the microscope from their relative positions in the local arrangement and their orientations. In our experimental setup, excitation light spot can be accurately focused onto the center of each rod via a red positioning hollow spot, as shown in Fig. 1(d). Typical UCL spectra obtained from several numbered single Ag-capped micron rods are shown in Fig. 2, which demonstrates that the UCL intensity from different rods fluctuates acutely: emitting weakly as for No. 9, or strongly as for No. 27. Meanwhile, the relative intensity of green UCL to red one (G/R) also varies from rod to rod in Sample.

In order to clarify the effects of Ag cap on UCL of micron rods, Ref-1 was designed as a reference to quantitate the enhancement,

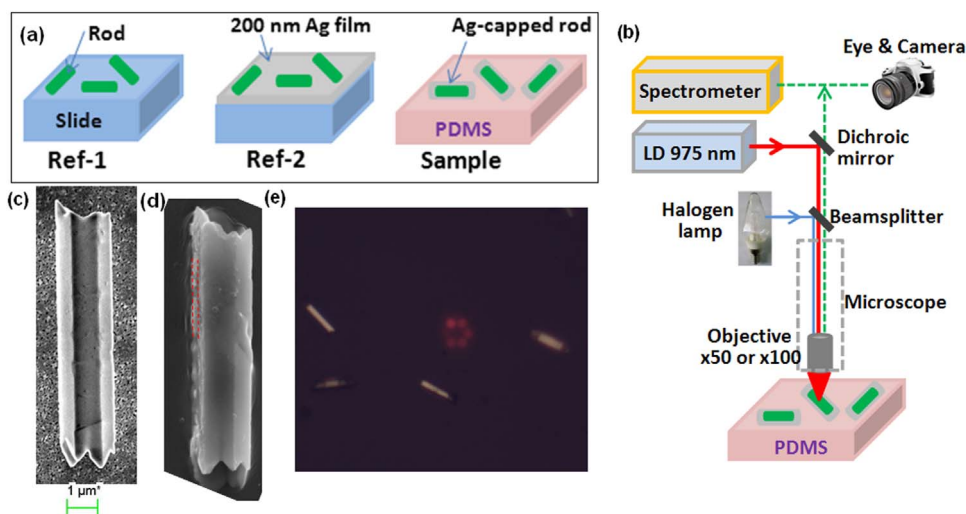


Fig. 1. Experimental information. (a) Schematic illustrations of the Ag-capped UC micron rods on PDMS (Sample) and two other structures (Ref-1 and Ref-2) for reference; (b) Experimental setup for the micro-spectral measurements of single micron rods; (c) and (d) SEM images of typical UC micron rods without and with Ag cap, (e) Dark field optical microscope image of the Ag-capped UC rods on PDMS.

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