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Enhancing the upconversion luminescence and photothermal conversion properties of ∼800 nm excitable core/shell nanoparticles by dye molecule sensitization

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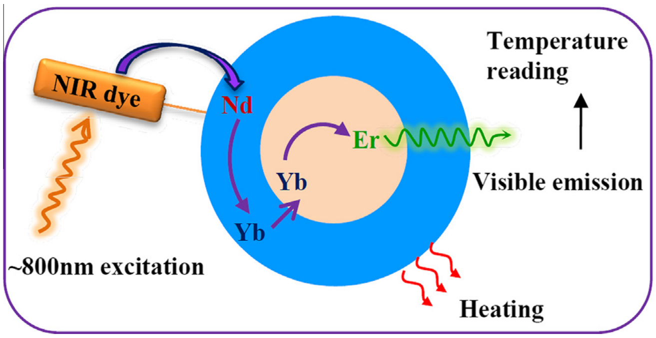
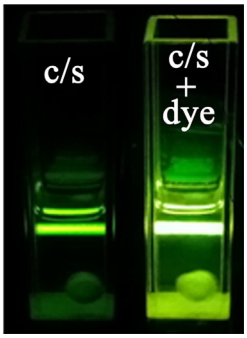
GRAPHICAL ABSTRACT





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ABSTRACT

Upconversion nanoparticles capable of strongly absorbing photons in a wide spectral range are highly desired for practical applications. In this work, IR-806 dye was used to increase the light absorptivity of $Nd^{3+}/Yb^{3+}/Er^{3+}$ tri-doped core/shell nanoparticles and then to enhance their upconversion luminescence under ∼800 nm excitation. The IR-806 dye exhibited more efficient energy transfer to Nd^{3+} ions than to Yb^{3+} ions for subsequent upconversion emission due to the increased spectral overlap between the dye emission and Nd^{3+} absorption. The influence of the Nd^{3+} concentration in the shell and the dye/-nanoparticle ratio on the dye-sensitization effect was also investigated. A maximum 28-fold overall enhancement in the emission intensity was achieved for $NaYF_4:Yb^{3+}/Er^{3+}@NaYF_4:Yb^{3+}/Nd^{3+}$ core/shell nanoparticles using dye sensitization. The dye-sensitized $NaYF_4:Yb^{3+}/Er^{3+}@NaYF_4:Yb^{3+}/Nd^{3+}$ core/shell nanoparticles also exhibited increased photothermal conversion capabilities and excellent temperature sensing properties, enabling their potential application in photothermal nanoheaters with real-time temperature monitoring under 808 nm single beam excitation.

1. Introduction

Upconversion nanoparticles (UCNPs), which can absorb near-infrared (NIR) light and emit visible light, exhibit great potential for applications ranging from bioimaging to photovoltaic technologies [1–3]. Although great advances have been achieved, some serious limitations still impede practical applications of UCNPs. Hexagonal (β) phase $NaYF_4:Yb^{3+}/Ln^{3+}$ (Ln = Er, Tm, Ho) UCNPs have been reported as the most efficient upconversion nanomaterials. However, due to the parity-forbidden nature of intra-4f transitions, the absorption band of the sensitizer Yb^{3+} is relatively narrow and

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located at ~980 nm. For imaging in a biological system, 980 nm laser sources usually cause strong water absorption and thus sample overheating, which can result in significant cell death and tissue damage. An effective method to solve this problem is the design of $Yb^{3+}/Nd^{3+}/Er^{3+}$ (Tm^{3+}) tri-doped core-only or core/shell UCNPs, which can successfully shift the excitation wavelength at ~980 nm to a more biocompatible wavelength at ~800 nm [4–10]. In these systems, the Nd^{3+} ions absorb photons at ~800 nm, whereas the Yb^{3+} ions act as a bridge, receiving the energy from the Nd^{3+} ions and transferring it to the emitter Er^{3+} or Tm^{3+}. These ~800 nm excitable UCNPs instead of traditional ~980 nm excitation can greatly increase the penetration depth into biological tissue and suppress unwanted overheating.

Upconversion materials capable of strongly absorbing photons covering a wide spectral range are highly desired for practical applications such as solar cell development. However, the absorption bands of Yb^{3+} and Nd^{3+} ions are incoherently weak and narrow, limiting their harvesting capacity to excitation photons. Zou et al. reported a design and synthesis of dye-sensitized $NaYF_4$:Yb^{3+}/Er^{3+} UCNPs, in which the carboxylic-modified cyanine dye acts as an antenna to absorb excitation energy across a broad wavelength range, which is then transferred to Yb^{3+} ions in UCNPs [11]. The dye-sensitized nanoparticles showed a remarkable upconversion luminescence (UCL) enhancement as a result of increased absorptivity and overall broadening of the absorption spectrum of the nanoparticles. The excitation band of Yb^{3+}-doped UCNPs can be further expanded by mixing various types of dye molecules [12]. Nevertheless, a large energy mismatch between dyes and Yb^{3+} ions occurs and limits the energy transfer process between them [11]. Recently, NIR dye sensitized $NaYbF_4$:Tm^{3+}@$NaYF_4$:Nd^{3+} core/shell UCNPs were reported by Chen et al., which showed a broad absorption range, a large absorption cross-section and considerably high quantum efficiency [13]. This finding demonstrated the feasibility of utilizing the energy transfer between NIR dyes and Nd^{3+} ions to enhance the UCL of Nd^{3+}-doped nanoparticles.

Despite recent advances, the influence of core/shell structures, lanthanide emitters and the spatial distribution of doped lanthanide ions on the energy transfer capability from NIR dyes to Nd^{3+} ions still deserves further study. In this paper, dye-sensitized $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Yb^{3+}/Nd^{3+} core/shell nanoparticles were prepared, and their UCL, temperature sensing and photothermal conversion properties were studied. Dye molecules act as antennas, absorbing excitation energy and transferring it to the emitter ions (Er^{3+}) in core/shell nanoparticles via an energy-cascading transfer pathway, that is, dye → Nd^{3+} (in the shell) → Yb^{3+} (in the shell and core) → Er^{3+} (in the core) [Fig. 1(a)]. More efficient energy transfer from the dye to Nd^{3+} was demonstrated than to Yb^{3+}, and a significantly enhanced UCL of Nd^{3+}-doped UCNPs upon ~800 nm excitation was realized. The effects of the Nd^{3+} concentration in the shell and the dye/nanoparticle ratio were also investigated.

2. Materials and methods

2.1. General chemicals

IR-780 iodide (98%), yttrium (III) acetate hydrate (99.9%), ytterbium (III) acetate tetrahydrate (99.9%), erbium (III) acetate hydrate (99.9%), neodymium (III) acetate hydrate (99.9%), ammonium fluoride (99.8%), sodium hydroxide (99.8%), methanol (>99.9%), oleic acid (90%) and 1-octadecene (90%) were obtained from Sigma-Aldrich. 4-mercaptobenzoic acid (90%), N,N-dimethylformamide (DMF, 99.8%), diethyl ether (AR grade) and chloroform (99.5%) were purchased from Aladdin. Ethanol (absolute) and hexane (AR grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received.

2.2. Synthesis of the IR-806 dye

The so-called IR-806 dye for the attachment to the nanoparticle surface was synthesized via the carboxylic acid functionalization of a cyanine dye, IR-780, according to a previously reported procedure [11]. IR-780 is commercially available and shows no obvious biotoxicity at low doses [14]. In a typical synthesis (Scheme S1), IR-780 (50 mg, 0.075 mmol), 4-mercaptobenzoic acid (23.1 mg, 0.15 mmol) and DMF (10 mL) were added to a 50 mL three-necked flask and stirred at room temperature under an argon flow for 12 h. Then, the solution was heated at 50 °C under vacuum to remove DMF, and the residual was dissolved in $CHCl_3$ (5 mL). After the solution was filtered through a 0.45 μm PTFE syringe filter, the product was precipitated by adding diethyl ether (20 mL). The precipitate was collected by centrifugation, washed with diethyl ether and dried under a vacuum to obtain the IR-806 crystals.

2.3. Synthesis of $NaYF_4$:Yb^{3+}/Er^{3+} core nanoparticles

Core and core/shell upconversion nanoparticles were synthesized by a general co-precipitation strategy using lanthanide acetates as precursors [15]. In a typical synthesis of core nanoparticles, 1 mmol of lanthanide acetates (Y/Yb/Er = 78:20:2) was added to a 100 mL three-necked flask containing oleic acid (6 mL) and 1-octadecene (15 mL). The mixture was then heated to 120 °C for 30 min with vigorous stirring to form a clear solution. After cooling down to 50 °C, a methanol solution (10 mL) containing NH_4F (4 mmol) and NaOH (2.5 mmol) was added, and the resulting solution was stirred for 30 min under an argon flow. The solution was then heated to 70 °C to remove excessive methanol. The solution was heated to 310 °C under an argon atmosphere for 90 min and then cooled down to room temperature. The nanoparticles were precipitated by the addition of ethanol and isolated via centrifugation. The as-precipitated core nanoparticles were washed several times with ethanol and re-dispersed in hexane.

2.4. Synthesis of $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Yb^{3+}/Nd^{3+} core/shell nanoparticles

To prepare the shell precursor solution, 1 mmol of yttrium, ytterbium and neodymium acetates with various mole ratios was added into 6 mL of oleic acid and 15 mL of 1-octadeceneand and was subsequently heated at 120 °C for 30 min. After the solution was cooled down to 50 °C, the as-synthesized $NaYF_4$:Yb^{3+}/Er^{3+} core nanoparticles (1 mmol) in 10 mL of hexane were added along with a methanol solution (10 mL) containing NH_4F (4 mmol) and NaOH (2.5 mmol). The resulting solution was stirred at 50 °C for 30 min and then heated at 70 °C to remove methanol. In the following, the solution was heated to 310 °C under an argon atmosphere for 90 min to prepare core/shell nanoparticles. After the solution was cooled down to room temperature, the obtained core/shell nanoparticles were collected and washed using the same procedure as that of core-only nanoparticles.

2.5. Preparation of the dye-sensitized upconversion nanoparticles

The IR-806 dye was weighed and dissolved in $CHCl_3$ to produce a concentration of 0.1 mg/mL. The as-synthesized core/shell nanoparticles were dispersed in $CHCl_3$ to form a colloid solution (1 mg/mL). $CHCl_3$ was chosen as the solvent because it can dissolve IR-806 very well, and the hydrophobic UCNPs can be dispersed in