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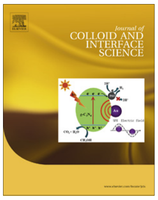

Upconversion color tuning in Ce^{3+}-doped $LiYF_4$:Yb^{3+}/Ho^{3+}@$LiYF_4$ nanoparticles towards ratiometric fluorescence detection of chromium (III)

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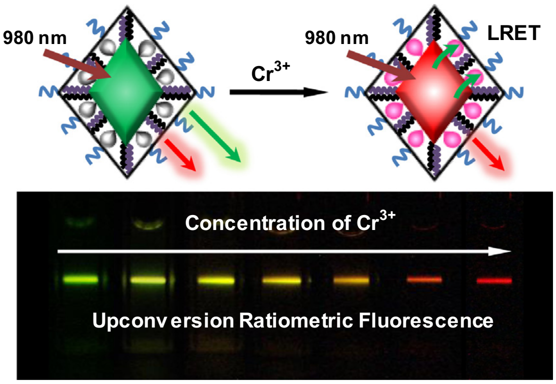
HIGHLIGHTS

- A dual-emission Ce^{3+}-doped $LiYF_4$:Yb^{3+}/Ho^{3+}@$LiYF_4$ upconversion nanoparticles were synthesized.
- The output color of the nanoparticles can be precisely manipulated by modulating the doping-concentration of Ce^{3+} ions.
- Cr^{3+}-responsive rhodamine derivative was assembled on the surface to fabricate the colorimetric probe by LRET process.
- A sequence of color change were obtained under 980 nm laser excitation, which could easily be visualized by the naked eye.
- This ratiometric probe is successfully applied to practical detection.

GRAPHICAL ABSTRACT

A ratiometric fluorescence sensor for Cr^{3+} detection has been developed based on luminescent resonance energy transfer in rhodamine derivative modified $LiYF_4$:Yb^{3+}/Ho^{3+}/Ce^{3+}@$LiYF_4$ upconversion nanoparticles.



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ABSTRACT

Ratiometric fluorescence sensor exhibits advantages of sensitive response, high anti-interference ability and naked eye visualization owing to multiple independent emission peaks utilized for results analysis. To achieve such multi-emission probe, the traditional methods have involved simple mixing of two emitters or tedious synthesis processes of hybrid material. However, these probes often have problems of inconstant emission strength ratio, low light-stability, and complicated synthetic process, which limit their applications in practical field. Herein, we report a single-structure Ce^{3+}-doped $LiYF_4$:Yb^{3+}/Ho^{3+}@$LiYF_4$ upconversion nanoparticles (UCNPs), which features two emission peaks in the green (at 540 nm) and red (at 640 nm) region under the excitation of 980 nm near infrared laser. Importantly, the red/green intensity ratio can be regulated by changing the doping level of Ce^{3+} to modulate output colors. Furthermore, a Cr^{3+}-responsive rhodamine derivative (CRD) was modified on the devised UCNPs surface to fabricate the colorimetric probe by luminescent resonance energy transfer (LRET) process. Upon addition of Cr^{3+} into the probe solution, the absorption peak of CRD at 560 nm is significantly enhanced, which greatly reduced the green emission, leading to an obvious color evolution from green

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to yellow to orange and to red with increasing the concentration of Cr^{3+}. This method is successfully applied to practical detection of Cr^{3+} ion in industrial waste water. The work reported here demonstrates a useful way to construct color-based visual assays.

1. Introduction

With the increasing demands for chemical/biological sensing, ratiometric fluorescent technologies have recently attracted more and more attentions, owing to their user-friendly operation, high sensitivity and excellent repeatability [1–6]. In a typical ratiometric fluorescent system, two non-overlapping emission peaks are always required and kept in a reasonable intensity ratio. When the target species is introduced into the fluorescent system, one of the emission intensity is decreased as working signal and the other is stable as internal reference, showing a concentration-dependent fluorescence intensity ratio change. This method can provide precise and quantitative determination of analyte due to the self-calibration of two emissions [7–9]. In principle, consecutive color variations of the ratiometric probe are governed under the color superposition principle of two selected colors. To obtain such dual-emission fluorescent materials, the ratiometric probes are usually constructed via simply mixing or covalent linking of luminescent materials, including quantum dots (QDs), carbon dots (CDs), nanoclusters (NCs), etc. For example, the mixed cyan CDs and red QDs have achieved for the dosage-sensitive visualization of As (III), while the linked blue CDs and red QDs which encapsulated into silica nanoparticle have obtained the quantification of blood glucose [10,11]. Unfortunately, the mixed probes often induce color separation in complex environment and the linked probe is difficult to synthesize in a suitable proportion, which limit their practical application.

Lanthanide-doped upconversion nanoparticles are capable of converting single wavelength, low-energy light to high-energy radiation (from ultraviolet to near-infrared region) through multiple photon process due to their ladder-like 4*f* orbital electron transitions [12–16]. The wavelength and intensity of upconversion emission are controlled by the types and concentrations of lanthanide ions, host lattices and particle infrastructure [17]. Especially, co-doping rare earth ions in one matrix could integrate multiple luminescent centers and regulate transfer pathways between different energy levels, which lead to multiple emission bands [18]. Notably, these influencing factors are strongly relied on the synthesis processes, thus the emission wavelength and intensity will remain when the lanthanide-doped materials are prepared. Therefore, upconversion material is a kind of ideal luminescent nanocrystals to construct ratiometric fluorescent probes.

In this work, we proposed the use of Yb^{3+}, Ho^{3+} and Ce^{3+} triply doped upconversion nanoparticles to obtain an optimum green/red (540 nm/640 nm) ratio of emission intensity in $LiYF_4$ host for ratiometric sensing. The doping concentration of Ce^{3+} ions, which is crucial for the emission color of the nanoparticles, has been precisely optimized. To demonstrate the potential possibility for ratiometric detection, we chose Cr^{3+} ions sensing as an example. Chromium is a trace metal element of human body for physiological function, but excessive intake of chromium ions is seriously harmful to the health. Here, using 1 mol% Ce^{3+}-containing $LiYF_4$ nanoparticles as energy donor, a Cr^{3+}-responsive rhodamine derivative was assembled on the surface to quench the green emission of Ho^{3+} by LRET process. Meanwhile, the red emission of Ho^{3+} acted as an internal standard, causing a sequence of color change under the excitation of 980 nm laser, which could easily be distinguished by naked eye. Compared with the classical analysis method (including atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, X-ray fluorescence spectrometry and so on), the ratiometric probe is low-cost and time-saving, which can be used as a convenient visual indicator for the detection of Cr^{3+} in industrial waste water. In addition, the sensitive and selective probe report here is suitable for real-time and on-site detection.

2. Materials and methods

2.1. Chemicals and materials

Oleic acid (OA, 90%), 1-octadecene (ODE, 90%), *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDC), poly (maleic anhydride-*alt*-1-octadecene) ($PMHC_{18}$) and trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich. Chromium (III) chloride hexahydrate, ethanol, hydrochloric acid, sodium hydroxide, cyclohexane, rhodamine B, hydrazine hydrate and furfural were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The NH_2-mPEG (2 kDa) was purchased from Shanghai Yare Biotech. $RE(CF_3COO)_3$ ($RE = Y^{3+}$, Yb^{3+}, Ho^{3+}, Ce^{3+}, Li^+) were synthesized via dissolving rare earth oxides in TFA, and followed by the evaporation of the excess water and acid. All the ultrapure water was produced using Millipore purification system.

2.2. Synthesis of $LiYF_4:Yb^{3+}/Ho^{3+}/Ce^{3+}@LiYF_4$ core-shell UCNPs

The nanoparticles were prepared by modifying the thermal decomposition process from the literature [19,20]. Briefly, 0.2 mmol of $Yb(CF_3COO)_3$, 0.02 mmol of $Ho(CF_3COO)_3$, x mmol of $Ce(CF_3COO)_3$ and (0.78-x) mmol $Y(CF_3COO)_3$ were added into a 50 mL three-neck flask with 10 mL OA and 10 mL ODE under stirring, then the mixture was heated to 120 °C under vacuum for 1 h to obtain transparent solution. After that, the mixture was directly heated to 300 °C and kept for 1 h in Argon atmosphere to form the core particles. The procedure of the shell growth was performed by shell-precursor injection. Typically, 1 mmol $Y(CF_3COO)_3$ and 1 mmol $Li(CF_3COO)_3$ were mixed with 10 mL OA and 10 mL ODE in a two-neck flask under vacuum at 120 °C for 1 h. Then, 1 mL of above precursor solution was injected into the core solution at 300 °C and ripened for 15 min. The injection was repeated 5 times to obtain a desired shell thickness. After cooled down naturally to room temperature, the core-shell UCNPs were collected by precipitation with acetone, wash by ethanol and re-dispersed in cyclohexane.

2.3. Synthesis of Cr^{3+}-responsive rhodamine derivative (CRD)

CRD was synthesized according to the reported literature by a modified procedure.[21] The synthetic route of the CRD was described in Scheme S1†. First, rhodamine B hydrazide (RBH) was prepared by reaction of rhodamine B with excess hydrazine hydrate. Then, 0.48 g (1 mmol) of RBH was dissolved in 20 mL ethanol with 0.1 g (1 mmol) of furfural and refluxed for 10 h until the pink solid was formed. The product was purified by recrystallization and characterized by ^1H NMR and HR-MS (see Supplementary material).