



Enhanced red emission of 808 nm excited upconversion nanoparticles by optimizing the composition of shell for efficient generation of singlet oxygen



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ARTICLE INFO

Article history:

Received 2 August 2017

Received in revised form

12 September 2017

Accepted 26 September 2017

Keywords:

Upconversion nanoparticles

Red/Green ratio

Upconversion luminescence intensity

Photosensitizer

Mesoporous silica

Singlet oxygen

ABSTRACT

With the aim to enhance the upconversion luminescence (UCL) intensity, much attention was paid to reduce the energy-back transfer from Er^{3+} ions to Nd^{3+} ions by constructing various kinds of multilayer upconversion nanoparticles (UCNPs). However, the energy-back transfer was difficult to be completely eliminated. Also, the thick shell of multilayer UCNPs is not favourable for effective Förster resonance energy transfer (FRET) in photodynamic therapy (PDT) system. Herein, an effective and facile method was applied to prepare UCNPs by optimizing the composition to largely enhance the red emission (at 660 nm) for efficient generation of singlet oxygen ($^1\text{O}_2$). In detail, the concentrations of Nd^{3+} ions and Yb^{3+} ions doped in the sensitizing shell were systematically researched to balance the energy back-transfer and the light harvest ability. The optimal emission and a relatively high Red/Green (R/G) ratio of $\text{NaYF}_4:\text{Yb,Er,Nd}@(\text{NaYF}_4:\text{Yb}_{0.1}\text{Nd}_{0.2})$ UCNPs were obtained simultaneously. Furthermore, the emission under 980 nm excitation demonstrated the energy back-transfer from Er^{3+} to Yb^{3+} ions was also notable which was largely ignored previously. Then, UCNPs were encapsulated into mesoporous silica shell, and the photosensitizer Chlorin e6 (Ce6) was covalently conjugated to form a non-leaking nanoplatform. The efficiency of $^1\text{O}_2$ generation obviously increased with the enhanced emission of UCNPs.

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1. Introduction

In recent years, rare-earth upconversion nanoparticles (UCNPs) have been widely investigated in diverse biomedical applications attributed to the unique advantages, such as high chemical stability, minimized auto-fluorescence background, high penetration depth and low biotoxicity [1–7]. Particularly for photodynamic therapy (PDT) [8–12], UCNPs are used as nanotransducers to convert deep tissue-penetration depth near-infrared (NIR) excitation to visible (VIS) or ultraviolet (UV) emission [13–16], and the fluorescence from UCNPs can activate the photosensitizers via the process of Förster resonance energy transfer (FRET) to generate singlet oxygen ($^1\text{O}_2$) for PDT [17–19].

Nonetheless, traditional UCNPs are typically sensitized by Yb^{3+} ions which only can be excited by the narrowband NIR excitation centered at 980 nm, which leads to a strong overheating effect due to significant water absorption [10,20,21]. Recently, Nd^{3+} doping can realize upconversion emissions of UCNPs with excitation at 808 nm where the water absorption is about 20 times lower than that of Yb^{3+} counterpart [22]. Meanwhile, the absorption cross section of Nd^{3+} is much larger than that of Yb^{3+} , and the efficient energy transfer from excited Nd^{3+} ions to Yb^{3+} ions can be up to 70% [22–24]. Therefore, much effort has been made to enhance the upconversion luminescence (UCL) intensity of Nd^{3+} sensitized UCNPs [25–28]. Recently, Yao et al. fabricated a kind of multilayer UCNPs with a transition layer to reduce the energy back-transfer between the Nd^{3+} ions and Er^{3+} ions [26]. Nevertheless, the synthetic process was too complex and difficult to control, and the thick shell of UCNPs is not favourable for effective FRET [29,30]. In fact, compared with reducing the energy back-transfer, the composition modulation is also very important for Nd^{3+} sensitized UCNPs due to the abundant energy levels and cross relaxations of the rare-earth ions.

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In this study, an effective and facile method was applied to synthesize the UCNP s with a relatively high Red/Green (R/G) ratio and enhanced red emission (at 660 nm). The red emission from UCNP s can overlap with the absorption band of the photosensitizer Chlorin e6 (Ce6) to efficiently activate Ce6 and produce $^1\text{O}_2$. Firstly, the $\text{NaYF}_4:\text{Yb,Er,Nd}$ (30/0.5/1 mol%) nanoparticles was prepared as emission core. Then, the concentration of Nd^{3+} ions and Yb^{3+} ions doped in the sensitizing shell were systematically investigated to optimize the UCL intensity (Scheme 1a). The energy back-transfer and light harvest ability effectively balanced through this strategy. Furthermore, a mesoporous silica shell was coated on the UCNP s, and the photosensitizer Ce6 was covalently conjugated to realize the FRET under 808 nm excitation (Scheme 1b). The $^1\text{O}_2$ production properties of mesoporous silica nanoparticles encapsulating Ce6 and UCNP s with different composition were characterized. The $^1\text{O}_2$ generation was largely improved due to the enhanced UCL intensity.

2. Experimental section

2.1. Materials

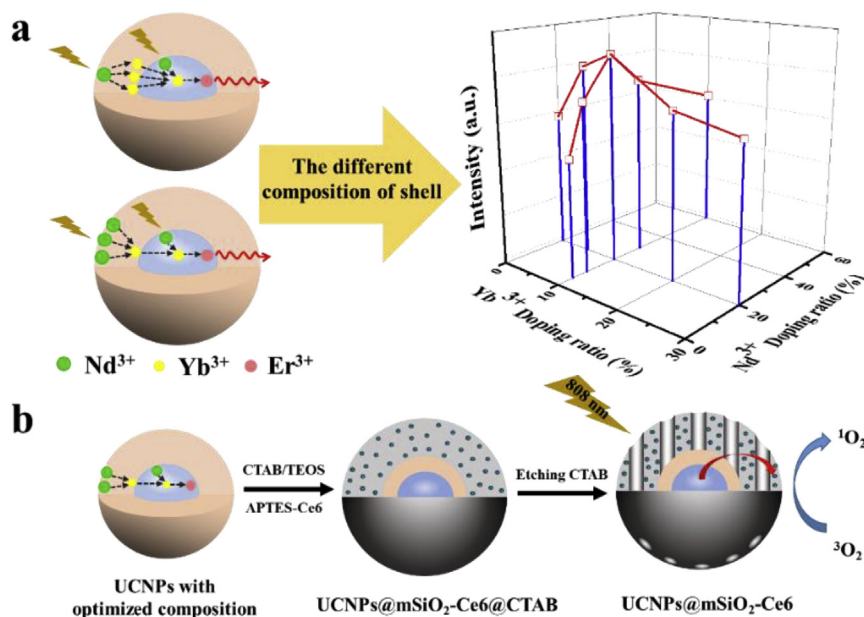
All reagents were analytical grade and used without further purification. Deionized water was used throughout all experiments. Erbium(III) acetate hydrate (99.9% trace metals basis), ytterbium(III) acetate hydrate (99.9% trace metals basis), yttrium(III) acetate hydrate (99.9% trace metals basis), neodymium(III) acetate hydrate (99.9% trace metals basis) and 1,3-diphenylisobenzofuran (DPBF) were purchased from Sigma-Aldrich. Tetraethyl orthosilicate (TEOS), (3-aminopropyl) triethoxysilane (APTES), hexadecyltrimethyl ammonium bromide (CTAB), oleic acid (OA), 1-octadecene (ODE), NaOH (98%) N-hydroxysuccinimide (NHS) and N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) were purchased from Aladdin company. NH_4F (98%), acetonitrile (95%), ethanol (99.7%), methanol (99.5%), dimethyl sulfoxide (DMSO) and cyclohexane (99.5%) were supplied by Jiangnan Chemical Technology Co. Ltd. (Tianjin China). Chlorin e6 (Ce6) was purchased from J&K Scientific Co. Ltd. (Beijing, China).

2.2. Preparation of $\text{NaYF}_4:\text{Yb,Er,Nd}$ emission core

Hexagonal $\text{NaYF}_4:\text{Yb,Er,Nd}$ (30/0.5/1) core was synthesized by using literature protocols with few modifications [31]. Firstly, 1.6 mmol $\text{Y}(\text{CH}_3\text{CO}_2)_3$, $\text{Yb}(\text{CH}_3\text{CO}_2)_3$, $\text{Er}(\text{CH}_3\text{CO}_2)_3$ and $\text{Nd}(\text{CH}_3\text{CO}_2)_3$ lanthanide acetates with desired amount were mixed with 30 mL ODE and 12 mL OA in a flask (100 mL). Then the resulting mixture was heated to 150 °C and maintained for 60 min at this temperature to remove possible oxygen and water. After the mixture was cooled down to 50 °C, 20 mL methanol solution containing 4 mmol NaOH and 6.4 mmol NH_4F was injected into the reaction vessel with vigorous stirring for 60 min at 50 °C. The methanol was evaporated by increasing the reaction temperature to 100 °C under vacuum. Subsequently, temperature of the reaction mixture was increased to 300 °C and kept for 2 h under argon atmosphere. After that the system was cooled down to room temperature under a flow of argon. Finally, the prepared core nanoparticles were precipitated by adding ethanol and washed with ethanol three times, then dispersed and stored in 10 mL cyclohexane for further use.

2.3. Preparation of $\text{NaYF}_4:\text{Yb,Er,Nd}@ \text{NaYF}_4:\text{Yb}_x\text{Nd}_y$ UCNP s with different composition

The shell precursor was prepared by mixing desired amount of $\text{Y}(\text{CH}_3\text{CO}_2)_3$, $\text{Nd}(\text{CH}_3\text{CO}_2)_3$ and $\text{Yb}(\text{CH}_3\text{CO}_2)_3$ (0.4 mmol in total) with 15 mL ODE and 6 mL OA in a flask (50 mL). Then the resulting mixture was heated to 150 °C and maintained for 60 min at this temperature to remove possible oxygen and water. After the mixture was cooled down to 50 °C, 5 mL prepared core nanoparticles solution was slowly added along with 10 mL methanol containing NaOH (1 mmol) and NH_4F (1.6 mmol) with vigorous stirring for 60 min at 50 °C. The cyclohexane and methanol were evaporated by increasing the reaction temperature to 100 °C under vacuum. Subsequently, temperature of the reaction mixture was increased to 300 °C and kept for 2 h under an argon atmosphere. After that the system was cooled down to room temperature under a flow of argon. Finally, the resulting core-shell nanoparticles were precipitated by adding ethanol and washed with ethanol three



Scheme 1. (a) Schematic representation for the formation of 808 nm excited UCNP s with different composition. (b) Functionalization of core-shell UCNP s with mesoporous silica and photosensitizer Ce6 and their FRET upon the excitation of 808 nm laser.

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