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Upconversion $NaGdF_4$ nanoparticles for monitoring heat treatment and acid corrosion processes of hair

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Abstract: Lanthanide-based upconversion core-shell $NaGdF_4$ nanocrystals with strong upconversion luminescence and biocompatibility were synthesized by the solvothermal method. The multicolor upconversion emission of these $NaGdF_4$ nanoparticles could be easily obtained by controlling the core-shell compositions. These multicolor core-shell $NaGdF_4$ upconversion nanocrystals could be employed as fluorescent probes for imaging the mouse hair, by which the porous and scalelike structure of the mouse hair were presented clearly. Meanwhile, it was directly shown by fluorescent signals that the mouse hair could resist the corrosion of the strong acid even when the concentration of hydrochloric acid was increased to 36.5%, but could not avoid the carbonization at high temperature of 400 ºC. This procedure based on upconversion fluorescent nanoprobes opens a novel route for investigating the basic physical structure and chemical properties of biological tissue and organism.

Keywords: upconversion; multicolor; imaging; mouse; hair; rare earths

Fluorescence imaging technology has been widely used for multicolor, multiplexed imaging *in vivo* and *in vitro* to investigate molecular information on biological tissues, change of physiologic parameters and complex biological process in cells or among cells[1–4]. Compared with the conventional biological imaging based on principle of slice transmission light, the fluorescent labeling is very desirable for cell imaging and monitoring organic analytes excretion due to intrinsic merits including high sensitivity, sharp emission spectra, and surface fluorescent imaging to avoid the slicing process[5,6]. Conventional fluorescence imaging technology was ever a powerful tool for imaging cells and tissues. However, single photon excitation process which converts high energy radiation to low energy visible fluorescence still has various inherent limitation for long term cell tracing and cell imaging, such as cell damage or protein denaturation when irradiated with high energy light for a long time[7–9]. Especially, unserviceable auto-fluorescence from tissues would lead to high noise to signal ratio. Organic dyes and fluorescent protein as nanoprobes based on two photons process have overcome these shortcomings to some extent, whereas low quantum yield, rapid chemical degradation, photobleaching existed, which limit their application in fluorescence imaging[10]. Inorganic semiconductor quantum dots (QDs) materials have been developed and used for imaging cell and tissues due to high quantum yield, broad ultraviolet (UV) excitation and good photostability. Nevertheless, their potential toxicity and chemistry instability hinder development in the field of bioimaging and clinical applications[11–13]. To avoid these defects of organic dyes and QDs, upconversion nanoparticle probes based on sequential absorption of two photons or multiphoton have received extensive attention[14–20].

Upconversion fluorescent nanoparticle (UCNPs) is a kind of desirable optical bioprobes for imaging cells and clinical therapy owing to following merits. The tissues penetration depth can reach 3.2 cm when using NIR irradiation as excitation source[21]. Moreover, photobleaching will be avoided. At present, the emission spectrum of UCNPs can be tuned easily for multicolor by some strategies[22–25]. For instance, Zhang′s group have reported that multicolor upconversion could be achieved by encapsulating organic dyes and quantum dots in core-shell nanospheres, which have application in cell labeling[26]. *In vivo* multicolor biomedical imaging using UCNPs based on different Ln^{3+} dopants was also investigated by Liu et al.[2]. Nevertheless, by constructing a shell layer on the surface of the core nanoparticles, up-

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conversion efficiency of nanoparticles can be improved exponentially. The upconversion emission can be tuned in a large range with high efficiency. What′s more, the deleterious cross relaxation process was reduced to larger extent after separating the appropriate lanthanide ions in the core and the shell layer because the concentration quenching effect can be minimized by applying core-shell structure[27]. To our best knowledge, by controlling gadolinium (Gd^{3+}) sublattice-mediated energy migration employing a well-defined core-shell structure, upconversion luminescence (UCL) of lanthanide activators without long-lived intermediary energy states can be successfully realized for multicolor imaging, which has rarely been reported[28].

In this work, we tuned the upconversion nanoparticles to generate four different colors under the single wavelength pumping by controlling the core-shell composition and energy migration between core-shell. The resultant different colors of UCNPs were functionalized with PEG hydrophilic polymer to afford water solubility and biocompatibility[29], which were applied for multicolor imaging of the living mice and mouse hair. Meanwhile, with assistance of UC fluorescent signals, we tried to address whether the porous and scalelike structure of the mouse hair was destroyed under the extreme environment (e.g., the strong acid, high temperature) or not. This work demonstrated that upconversion fluorescent nanoprobes are promising for future multiplexed imaging and diagnose under the single-wavelength pumping[30].

1 Experimental

1.1 Materials

Oleic acid (OA), 1-octadecene (ODE), polyethylene glycol (PEG), NaOH, NH_4F and methanol were obtained from Sigma Aldrich, which were used directly without further purification. All rare earth oxides were of 99.99%. RE_2O_3 (RE=Gd, Lu, Yb, Er, Tm, Eu, and Tb) were purchased from Sigma Aldrich. Rare earth chloride $RECl_3$ solution was prepared by dissolving the corresponding rare earth oxides in hydrochloric acid solution.

1.2 Synthesis of $NaGdF_4$:Yb/Tm (Er) core nanoparticles

In this synthesis, the core nanoparticles, Yb^{3+}, Er^{3+}/Tm^{3+} codoped $NaGdF_4$ were synthesized by the solvothermal method. $GdCl_3$ (0.32 mmol), $YbCl_3$ (0.072 mmol) and $ErCl_3$ (0.008 mmol) in deionized water and added to a 50 mL flask containing ODE (12 mL) and OA (4 mL). The mixture was slowly heated to 160 ºC under an argon atmosphere to remove residual water and was kept for 30 min, the system was then cooled to room temperature with flowing of argon. Afterwards, a solution (5 mL) containing 1.5 mmol NH_4F and 1 mmol NaOH dissolved in methanol was slowly added and stirred for another 30 min at a temperature of 50 ºC. After the methanol was evaporated, the mixture was heated to 310 ºC for 60 min in the presence of argon. After cooling to room temperature naturally, the products were collected by adding an excess amount of cyclohexane and centrifuged at 10000 r/min, and washed repeatedly with a 1:1 mixture of ethanol/H_2O, finally re-dispersed in 5 mL of cyclohexane for further experiments.

1.3 Synthesis of $NaGdF_4$:Yb/Tm@$NaGdF_4$:X core-shell nanoparticles

When the above-mentioned experiment was carried out, a mixture solution of 0.4 mmol $LnCl_3$ (Ln=Gd^{3+}, Eu^{3+}/Tb^{3+}) water solution and 16 mL of ODE/OA (v/v=3:1) were degassed at 160 ºC with constant stirring for 30 min. Shortly thereafter, the $NaGdF_4$:Yb^{3+}/Tm^{3+} core in cyclohexane was then added together with 5 mL methanol solution of NH_4F (1.5 mmol) and NaOH (1 mmol) and the resultant solution was stirred at 50 ºC for 30 min under to evaporate the methanol from the reaction mixture, the resulting solution was then heated to 315 ºC and kept at this temperature for 25 min and then cooled down to room temperature. Addition of 15 mL mixture solution of cyclohexane and ethanol was carried out and followed with centrifugation at 10000 r/min, and re-dispersed in cyclohexane for further use.

1.4 Characterization

Transmission electron microscopy (TEM) was conducted on a JEM 3010 high resolution transmission electron microscope operating at 200 kV. The prepared nanoparticles were characterized by placing a drop of cyclohexane solution on the surface of copper grid. Luminescence spectra were recorded at room temperature by using a Hitachi F-2700 spectrophotometer with a 980 nm laser as the excitation source. The UCL images of hair were obtained by a confocal laser scanning microscope equipped with a Tucsen H-694CICE digital camera. All optical measurements were performed at room temperature.

2 Results and discussion

A solvothermal method was adopted for synthesizing $NaGdF_4$ core nanoparticles with the doping of Yb^{3+}/Er^{3+} or Yb^{3+}/Tm^{3+} ionic pairs, then the active shell $NaGdF_4$:X^{3+} (Tb^{3+}, Eu^{3+}) was coated on their surface through a seed-mediated process. To reveal the phase and size control, these nanoparticles with surface modification were characterized by TEM and high-resolution TEM (HRTEM). It can be observed from Fig. 1(a) that $NaGdF_4$:Yb^{3+}/Tm^{3+} core nanoparticles have an average diameter of ~12 nm, hexagonal crystal facets, and good crystallinity. After being coated with $NaGdF_4$:X^{3+} (Eu^{3+},

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