



Water-soluble Yb³⁺, Tm³⁺ codoped NaYF₄ nanoparticles: Synthesis, characteristics and bioimaging

Huan Chen, Xuesong Zhai, Duo Li, Lili Wang, Dan Zhao*, Weiping Qin*

State Key Laboratory on Integrated Optoelectronics, College of Electronic Science & Engineering, Jilin University, Changchun 130012, China

ARTICLE INFO

Article history:

Received 15 March 2011

Received in revised form 8 August 2011

Accepted 9 August 2011

Available online 7 September 2011

Keywords:

NaYF₄

Upconversion

Water soluble

Nanoparticles

ABSTRACT

Water soluble NaYF₄ nanocrystals codoped with 20 mol% Yb³⁺, 0.5 mol% Tm³⁺ were prepared by a facile solvothermal approach using polyvinylpyrrolidone (PVP) as a surfactant. The upconversion NaYF₄ nanocrystals were pure cubic phase with an average size of ~40 nm. They could be well redispersed in water to form a clearly transparent solution without obvious precipitation. With the excitation of a 980-nm diode laser, the nanocrystal solution presents bright violet and blue upconversion luminescence. These upconversion nanoparticles (UCNPs) were incubated with HeLa cells at 37 °C for 24 h, and bright blue upconversion luminescence were observed from the UCNPs endocytosed into the HeLa cells on a microscope equipped with a 980-nm fiber laser. These results indicated that the UCNPs had potential applications for biological imaging as luminescent probes.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Upconversion (UC) is a nonlinear optical process that long-wavelength light can be converted to short-wavelength light by absorbing two or more pump photons [1]. UC materials have been widely used in many fields, including all-solid-state laser, full color display, optical communication, bio-labeling and so on [2,3]. Very recently, lanthanide (Ln)-doped UC nanoparticles (UCNPs) have attracted great attention as luminescent probes for bioimaging applications due to their remarkable advantages, such as large anti-Stokes shifts, narrow emission bandwidth, long fluorescence lifetime, and excellent photostability [4–7]. Compared with down-conversion probes, such as fluorescent organic dyes and quantum dots, the Ln-doped UC probes excited with near-infrared (NIR) light suffer much less the background autofluorescence that is usually encountered by ultraviolet (UV) pumping [8,9]. It also reaps the benefit of deep penetration into biological tissue by using a pumping light in the biological optical window of 800–1200 nm [10,11]. Furthermore, compared with high-energy UV excitation, low-energy NIR has the minimum photo-damage to the biological specimens [12].

NaYF₄ has been reported as the most efficient Ln-doped UC host material [13]. Under the 980 nm excitation, visible or UV emissions can be obtained via codoping Yb³⁺ ions as sensitizers, Tm³⁺ ions, Er³⁺ ions, or other rare earth (RE) ions as activators [14,15].

However, the RE ions codoped NaYF₄ materials should have the following properties in order to meet the demands as luminescent probes: (1) small size of sub-50 nm; (2) high dispersibility in water; (3) good biocompatibility; (4) strong UC luminescence in aqueous solutions [16,17]. It is worth noting that good water solubility and strong UC luminescence are especially the key factors. Li's group prepared oleic acid (OA)-capped UCNCs and used Lemieux-von Rudloff reagent to oxidize the C=C double bond of OA and then obtained the water soluble nanocrystals [18]. Zhang's group synthesized silica-coated polyvinylpyrrolidone (PVP)/NaYF₄ nanocrystals which could dispersed in some of the most commonly used solvents, from weakly polar chloroform to strongly polar water [19]. However, it is still a challenge to synthesize UCNPs used as luminescent probes with good aqueous dispersibility and strong UC luminescence intensity.

In this paper, we report on water soluble, cubic phase NaYF₄: 20 mol% Yb³⁺, 0.5 mol% Tm³⁺ UC nanocrystals prepared by a facile solvothermal method using PVP as the surfactant. These nanocrystals have an average size of ~40 nm with a narrow size distribution and can be well dispersed in water to form a clearly transparent solution. Under 980 nm excitation, the solution shows bright blue and violet emission that can be clearly seen with naked eye in day light. The HeLa cells could be labeled using these UCNPs as luminescent probes. These results indicated that the UCNPs had potential applications in biological field as luminescent probes.

2. Experimental

The initial chemicals, including Y₂O₃, Yb₂O₃, Tm₂O₃ (all with purity > 99.99%, Shanghai Shabo Chemical Technology Co., Ltd. China), hydrochloric acid (HCl,

* Corresponding authors. Tel.: +86 0431 85168241 8325;

fax: +86 0431 85168241 8325.

E-mail addresses: dzhao@jlu.edu.cn (D. Zhao), wpqin@jlu.edu.cn (W. Qin).

37 wt%), ethylene glycol (EG, AR), polyvinylpyrrolidone K-30 (PVP, 58,000 g/mol) and sodium fluoride (NaF, AR), were used without further purification.

2.1. Synthesis of sample

Y_2O_3 , Yb_2O_3 , and Tm_2O_3 were dissolved in dilute hydrochloric acid to form $RECl_3$ ($RE=Y, Yb, \text{ and } Tm$) solutions. After excess HCl and water were completely evaporated, the as-produced $RECl_3$ powders were dispersed in EG. 1 mmol $RECl_3$ (79.5 mol% YCl_3 , 20 mol% $YbCl_3$, and 0.5 mol% $TmCl_3$) solutions were mixed together and 0.5 g PVP K-30 was added under stirring (the exact ratio of PVP to RE^{3+} is 1/116). This solution was labeled as solution A. 0.21 g NaF (the molecular ratio of F^- to RE^{3+} is 5/1) was dissolved in EG, then this NaF solution was added dropwise to the solution A. This mixture was kept stirring for at least 30 min, then it was transferred into a polytetrafluoroethylene autoclave and reacted at 150 °C for 24 h. After cooling to room temperature, the products were obtained by centrifugation and washed with deionized water and ethanol. To remove the residual NaF completely, the products should be washed with warm deionized water for several times. A part of precipitation was dried at 60 °C for 2 h and the other was redispersed in deionized water by ultrasonic treatment to get transparent solution.

2.2. Cell labeling with UCNPs

The HeLa cells were cultured (at 37 °C, 5% CO_2) on glass chamber slides in PRMI (Roswell Park Memorial Institute) 1640 medium containing 10% fetal bovine serum and 1% penicillin/streptomycin overnight in an incubator (Sanyo MCO-20AIC) for 24 h. The cells were gently washed three times with phosphate buffer solution (PBS). Then the HeLa cells were incubated with 300 $\mu\text{g}/\text{mL}$ UCNPs for another 24 h in CO_2 incubator. After washing three times with PBS to remove excess UCNPs, the cells were imaged by an Olympus IX71 microscope equipped with a 980-nm fiber laser.

2.3. Measurements

The XRD analysis was carried out with a powder diffractometer (Model Rigaku RU-200b), using Ni-filtered $Cu\ K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with 200 mA current and 50 kV voltage across the tube to generate powerful X-ray. The XRD measurement was performed at a scan rate of $18^\circ \text{ min}^{-1}$ and step size of 0.02° . The morphology of the nanocrystals was investigated by FE-SEM (JEOL, JSM-6330F) and TEM (H-8100 200KV). A 2 W 980 nm continuous wave (CW) diode laser was used as the excitation source to study the UC luminescence of the sample. Their UC emission spectra were recorded with a fluorescence spectrometer (Hitachi F-4500). The UC luminescent pictures of the aqueous solution were taken by a Nikon digital camera (D300s). All the measurements were performed at room temperature.

3. Results and discussion

The XRD pattern of the $NaYF_4: 20 \text{ mol\% } Yb^{3+}, 0.5 \text{ mol\% } Tm^{3+}$ sample is shown in Fig. 1, where the diffraction peaks are in good agreement with the data of cubic-phase $NaYF_4$ nanocrystals (JCPDS No. 6-342, $a = 5.448 \text{ \AA}$), and there no other peaks of impurities has been detected. It indicates that the products is single-phase pure cubic $NaYF_4$ crystals and demonstrates the highly crystalline nature of the nanocrystals. Although the as-prepared sample is cubic phase which has been reported to be less efficient than hexagonal-phase $NaYF_4$, the UCNPs we synthesized still has strong UC luminescence intensity. Fig. 2(a) and (b) shows the SEM and TEM images of the

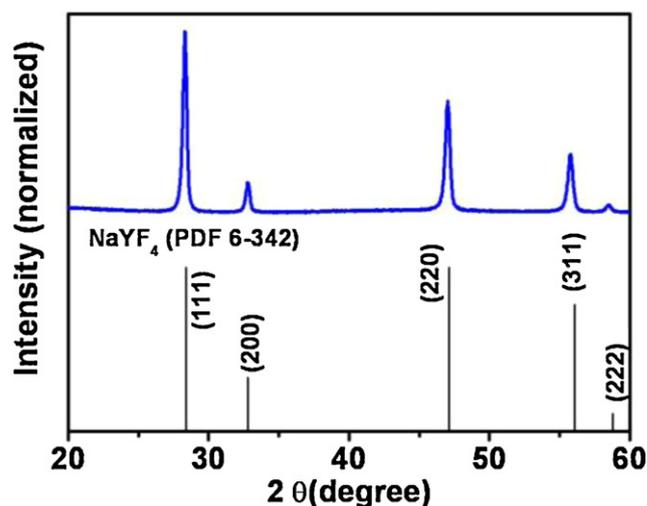


Fig. 1. (a) XRD pattern of the as-prepared UCNPs and standard data of cubic-phase $NaYF_4$ (JCPDS No. 6-342).

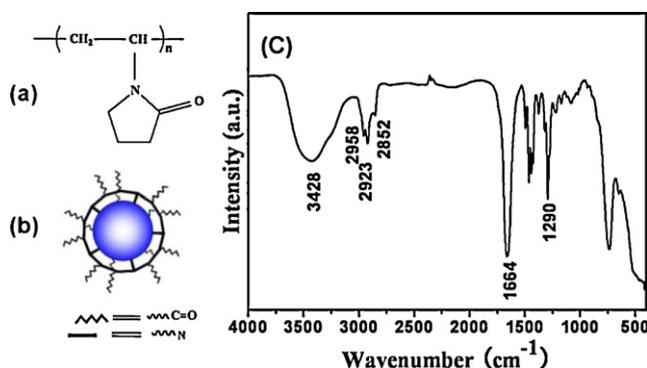


Fig. 3. (a) Molecular structure of PVP. (b) Scheme of the surface of PVP-modified UCNPs. (c) FTIR spectrum of the PVP-modified UCNPs.

cubic phase $Yb^{3+}-Tm^{3+}$ codoped $NaYF_4$ nanocrystals. In the SEM image, we can see that the nanoparticles have small size contribution. In TEM image, it can be confirmed that the as-prepared UCNPs have an average size of $\sim 40 \text{ nm}$. The small size of the nanoparticles sufficiently satisfies the demands of bio-applications as luminescent probes.

The molecular structure of PVP is given in Fig. 3(a). It is known that both the nitrogen and oxygen atoms have lone pair electrons which can combine with the empty orbital of metal ions. That

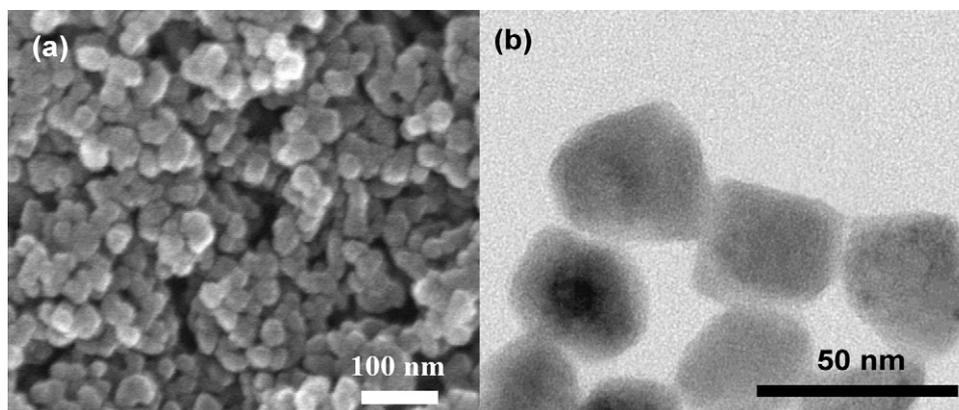


Fig. 2. (a) SEM and (b) TEM images of the UCNPs.

Download English Version:

<https://daneshyari.com/en/article/1616611>

Download Persian Version:

<https://daneshyari.com/article/1616611>

[Daneshyari.com](https://daneshyari.com)