Journal of Colloid and Interface Science 468 (2016) 300–306

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

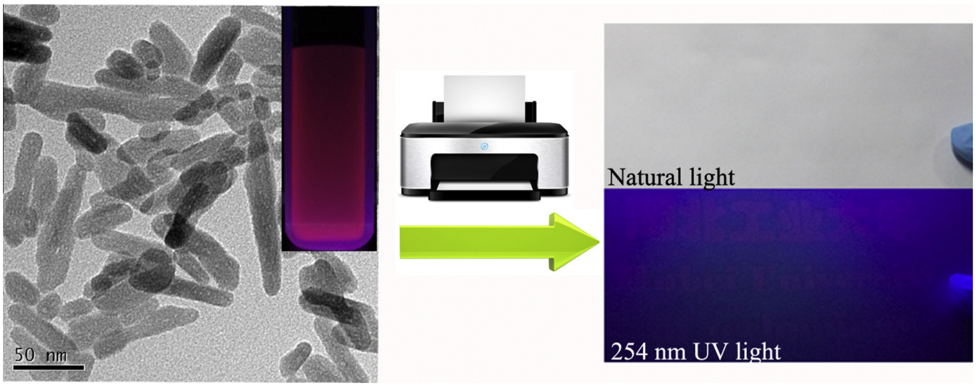
journal homepage: www.elsevier.com/locate/jcis

Large-scale synthesis of water-soluble luminescent hydroxyapatite nanorods for security printing

Xiaohu Chen [c,1], Xiaoying Jin [a,1], Junjun Tan [a,*], Wei Li [b], Minfang Chen [b], Lan Yao [c], Haitao Yang [c]

[a] School of Chemistry and Chemical Engineering, Hubei University of Technology, Wuhan 430068, Hubei, PR China
[b] School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, PR China
[c] School of Pulp and Paper Engineering, Hubei University of Technology, Wuhan 430068, Hubei, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 November 2015
Revised 28 January 2016
Accepted 30 January 2016
Available online 1 February 2016

Keywords:
Hydroxyapatite nanorods
Europium doping
Colloidal stability
Luminescence
Security printing

ABSTRACT

Luminescent hydroxyapatite nanoparticles, which have excellent biocompatibility, excellent photostability, and strong fluorescence, have received increasing attention as bioprobes in cell imaging. However, they are also excellent candidates for use in ink-jet security printing. Successful products for related applications usually require highly crystalline, mono-dispersible hydroxyapatite nanorods with good colloidal stability and high fluorescence in aqueous media. These requirements are hard to simultaneously satisfy using most synthetic methods. In this paper, we report a simple and versatile hydrothermal method that incorporates the use of sodium citrate to prepare water-dispersible Eu^{3+}-doped hydroxyapatite nanorods. The hydroxyapatite nanorods obtained using this method are highly crystalline rod-shaped particles with an average length of 50–80 nm and an average diameter of 15–30 nm. Dispersions of these hydroxyapatite nanorods, which are transparent with a slightly milky color under natural light and a bright red color when excited with 241 nm UV light, display zeta potentials of −35 mV and hydrodynamic diameters of 120 nm. These dispersions remain colloidally stable for a few months. Dispersions with these properties could be easily applied to security printing for confidential information storage and anti-counterfeiting technologies.

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[*] Corresponding author.
E-mail address: tanjunjun_martyr@126.com (J. Tan).

[1] Xiaohu Chen and Xiaoying Jin contributed equally to this paper.

http://dx.doi.org/10.1016/j.jcis.2016.01.078
0021-9797/

1. Introduction

Because of its excellent biocompatibility, biological activity, and strong ion exchange capacity, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), the mineral component of bone and teeth, is widely used in fields such as bone tissue engineering [1,2], heavy metal ions absorption [3,4], protein separation [5,6] and drug carriers [7,8]. Because calcium ions and lanthanide ions have similar atomic radii, hydroxyapatite nanocrystals are a good host material for lanthanide doping, which may endow the material with fluorescent properties [9,10]. Because of these advantages, lanthanide-doped hydroxyapatite nanoparticles have attracted considerable attention not only as bioprobes in cell imaging, but also as excellent candidates for ink-jet security printing [11–20]. Many attempts have been made to develop synthetic strategies that will provide materials suitable for that purpose, including hydrothermal [21–26], chemical precipitate [27], microwave [28–30] and ultrasound [31] methods.

In these synthetic strategies, the desired products are highly crystalline, mono-dispersible hydroxyapatite nanorods with good colloidal stability and high fluorescence in aqueous media. These materials would be useful in related applications, especially for ink-jet printing. However, in most of the synthetic strategies mentioned above, the focus was restricted to one aspect alone, such as morphology, colloidal stability, fluorescence performance, or crystallinity of the hydroxyapatite particles. Few studies can be found that simultaneously achieve all of the desirable characteristics listed above.

It has recently been recognized that there is an abundance of citrate molecules in bone tissue—about 5.5 wt% of the organic matter in bone—and that most of these molecules are on the apatite surface [32]. A density of about one molecule per two square nanometers of crystalline apatite surface has been determined using solid state NMR analysis of natural bone [33]. These citrate molecules play very important roles in facilitating the dispersion of hydroxyapatite nanorods in bone tissue and in controlling the growth of apatite crystals. Our recent work shows that citrate molecules, which have excellent biocompatibility, strong ability to bind with calcium ions, and great dispersing ability, can be used as a rapid, scalable, and chemically green processing aid in the synthesis of water soluble hydroxyapatite nanorods [34,35]. The crystallinity, morphology, size and colloidal stability of hydroxyapatite nanorods can be easily tuned by controlling the hydrothermal conditions. Moreover, processing time can be greatly reduced by increasing the hydrothermal temperature. In view of these points, we believe that these types of treatments could be introduced for the large-scale synthesis of water-soluble hydroxyapatite nanorods exhibiting high fluorescence. These nanorods could be applied to ink-based printing for security information storage and anti-counterfeiting technologies. To the best of our knowledge, the use of Eu^{3+}-doped hydroxyapatite nanorods for security printing has not previously been reported.

Inspired by the studies mentioned above and our previous work [36–38], a systematic experimental evaluation of the effect of Eu^{3+} doping on particle morphology, crystallinity, colloidal stability and fluorescence performance of hydrothermally synthesized colloidal hydroxyapatite nanorods was conducted. The results of this evaluation and a proposed explanation of these effects are discussed. A preliminary evaluation of security printing using these materials was also conducted.

2. Materials and methods

2.1. Materials

Calcium chloride anhydrous ($CaCl_2$, $\geqslant$96.0%), sodium phosphate tribasic dodecahydrate ($Na_3PO_4 \cdot 12H_2O$, $\geqslant$98.0%), sodium citrate tribasic dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$, $\geqslant$99.0%), ethanol absolute (C_2H_6O, $\geqslant$99.7%), sodium hydroxide (NaOH, $\geqslant$96.0%) and nitric acid (HNO_3, 65.0–68.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Europium oxide (Eu_2O_3, 99.9% metals basis) were purchased from Aladdin Industrial Corporation. All chemicals were used as received, without further purification. Deionized water was used throughout. Stock solutions of $Eu(NO_3)_3$ were prepared by dissolving the respective Eu_2O_3 compounds in nitric acid with heating.

2.2. Methods

2.2.1. Preparation of colloidal hydroxyapatite nanorods

Colloidal hydroxyapatite nanorods were prepared using a hydrothermal method. In a typical experiment, a sodium citrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) solution of fixed concentration (0.033 M, 10 mL) was added, with continuous stirring, to an aqueous solution of $CaCl_2$ (0.05 M, 10 mL) and $Eu(NO_3)_3$ (x M, 10 mL) over 10 min. The doping level was calculated as $x/0.05$. Then, an aqueous solution of $Na_3PO_4 \cdot 12H_2O$ ($0.033 + x$ M, 10 mL) was added to the mixture with vigorous stirring over 15 min. After that, the mixed solution was transferred, as obtained, to a Teflon-lined stainless steel autoclave with a 50 mL capacity. The solution in the autoclave underwent hydrothermal treatment at 150 °C for 12 h. After the hydrothermal treatment, the autoclave was allowed to cool down naturally, and the resulting product was purified using a three-cycle centrifugation-washing (3700g) process with deionized water and ethanol. Finally, the purified product was re-dispersed in deionized water to form an aqueous dispersion. The pH was adjusted to pH 9 by the addition of 0.1 M NaOH. A portion of the sample was dried at 70 °C for 12 h to get powder for future characterization.

2.2.2. Printing with photoluminescent hydroxyapatite ink

A commercial paper that proved a suitable substrate for the hydroxyapatite nanorods and featured no background fluorescence under the UV lamp was chosen for use as the test paper. The aqueous dispersion of hydroxyapatite nanorods (50 mg/mL), acting as ink, was injected into a commercial ink-jet printer. The desired Chinese or English words were printed onto a piece of the test paper. The fluorescence images were obtained under 254 nm UV light.

2.3. Characterization

2.3.1. Wide-angle X-ray diffraction

The dried powders were characterized using X-ray diffraction with an X'Pert PRO X-ray diffractometer (PANalytical B.V., Almelo, Netherlands). Analyses were performed using a Cu Kα radiation (1.5406 A) source at 60 kV and 60 mA from 5° to 80° with a scan rate of 0.5°/min.

2.3.2. Transmission electron microscopy

The morphology of each product was inspected with a Tecnai G2/F20 Transmission Electron Microscope (TEM) (FEI, Hillsboro, OR, USA) using an accelerating voltage of 200 kV. Each colloidal hydroxyapatite nanoparticle sample was drawn by pipette and 1–2 droplets were placed onto the carbon side of a wholly carbon-coated Cu TEM-grid. The samples were dried before being attached to the sample holder on the microscope. Elemental analysis was conducted using TEM with an energy-dispersive X-ray spectrum (EDS, EDAX)

2.3.3. Zeta potential and DLS measurements

Zeta potential and particle size distribution measurements were performed using a nano-ZS90 Zetasizer (Malvern instruments Ltd.,