



# Comparative investigation on the crystal structure and cell behavior of rare-earth doped fluorescent apatite nanocrystals

Xiyu Li<sup>a</sup>, Haifeng Zeng<sup>b</sup>, Li Teng<sup>b</sup>, Haifeng Chen<sup>a,\*</sup>

<sup>a</sup> Department of Biomedical Engineering, College of Engineering, Peking University, No. 5, Yiheyuan Road, Haidian District, Beijing 100871, China

<sup>b</sup> Cranio-Maxillo-Facial Surgery Department 2, Plastic Surgery Hospital of Peking Union Medical College & Chinese Academy of Medical Sciences, Beijing 100144, China

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## ABSTRACT

Terbium (Tb) doped fluorapatite (FA:Tb) and hydroxyapatite (HA:Tb) crystals are hydrothermally synthesized. Their composition, crystal structure, fluorescence and biological properties are investigated. The Tb-doped crystals are in nanoscale and present a uniform slender morphology. The doping of Tb<sup>3+</sup> ions can promote the preferential growth of apatite nanocrystals along the *c*-axis (002) direction, and cause the binding energy to increase for FA:Tb<sup>3+</sup> crystals or decrease for HA:Tb<sup>3+</sup> crystals. The FA crystal structure tends to combine more Tb<sup>3+</sup> ions than the HA crystal structure, and shows a stronger green fluorescence. Four Tb-doping lattice models along the apatite hexagonal structure are proposed, revealing a necessity for coexistent substitution mechanism of (Ca<sub>7</sub>Tb<sub>2</sub>)(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, (Ca<sub>6</sub>Tb<sub>2</sub>Na<sub>2</sub>)(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, (Ca<sub>9</sub>Tb)(PO<sub>4</sub>)<sub>6</sub>(OH)O, and (Ca<sub>8</sub>TbNa)(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>. The Tb-doped apatite nanocrystals exhibit bright fluorescence, good cytocompatibility and excellent cell imaging capacity, providing feasibility for imaging and tracking of cells with multilineage differentiation.

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## 1. Introduction

The mineral phase of human calcified tissues is mainly composed of nanoapatite crystals [1]. Synthetic apatite, including hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, HA) and fluorapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub>, FA), has a similar hexagonal structure to biological apatite, and the Ca<sup>2+</sup> sites are easy to be substituted by many other ions, such as Mg<sup>2+</sup>, Sr<sup>2+</sup>, Na<sup>+</sup>, Al<sup>3+</sup>, etc. [2,3]. Due to the similarity in composition or structure, both HA and FA possess good biocompatibility and have been widely used as defect fillers of bones and teeth [4,5]. In recent years, some rare-earth doped materials are found to emit fluorescence when excited by UV or blue light [6,7]. The hexagonal structure of apatite crystals may be dominant in rare-earth doping and keeping thermal and fluorescence stabilities [8,9].

The trivalent lanthanide ions are sensitive to the chemical environments involved [10]. The lanthanide fluorescence has advantage over organic luminophores subjected to photobleaching [11], or semiconductor quantum dots with potential toxicity of Cd/Se and short circulation half-time [12]. Terbium (Tb) doped materials have been reported to generate green fluorescence [13,14]. Although the preparation method and fluorescence properties of

these Tb-doped materials were studied broadly, the effects of Tb<sup>3+</sup> ions on the crystal structure, lattice occupation and cell proliferation are not investigated in detail, and not compared between HA and FA nanocrystals. In order to reasonably express the incorporation mechanism of Tb<sup>3+</sup> ions into the apatite lattice and explore the effect of Tb<sup>3+</sup> doping on the crystal structure and cell proliferation, a doping molar ratio, 1.7/8.3, of terbium relative to calcium in a unit cell was chosen in this experiment.

## 2. Experimental

Two kinds of Tb-doped apatite nanocrystals were hydrothermally synthesized, and all chemicals were of analytical grade. For HA:Tb<sup>3+</sup> nanocrystals: octadecylamine (0.5 g) was dissolved in oleic acid (4 mL) and ethanol (16 mL) under magnetic stirring in a Teflon-lined autoclave (50 mL). Then aqueous solution of Ca(NO<sub>3</sub>)<sub>2</sub> (0.28 M, 7 mL), Tb(NO<sub>3</sub>)<sub>3</sub> (0.20 M, 2 mL), and Na<sub>3</sub>PO<sub>4</sub> (0.20 M, 7 mL) was added. For FA:Tb<sup>3+</sup> nanocrystals: additional NaF (0.24 M, 2 mL) was added. Afterwards, the mixture was agitated for 10 min, and hydrothermally treated at 160 °C for 16 h. After cooling to room temperature naturally, the white precipitate collected by centrifugation (10 min at 4000 rpm) was fully washed and freeze-dried. These nanocrystals were used for evaluation of cell proliferation via MTT assay and cell imaging. The detailed

\* Corresponding author. Tel.: +86 10 62754396.

E-mail address: [haifeng.chen@pku.edu.cn](mailto:haifeng.chen@pku.edu.cn) (H. Chen).

description of materials and methods can be found in the part of [Supplementary materials](#).

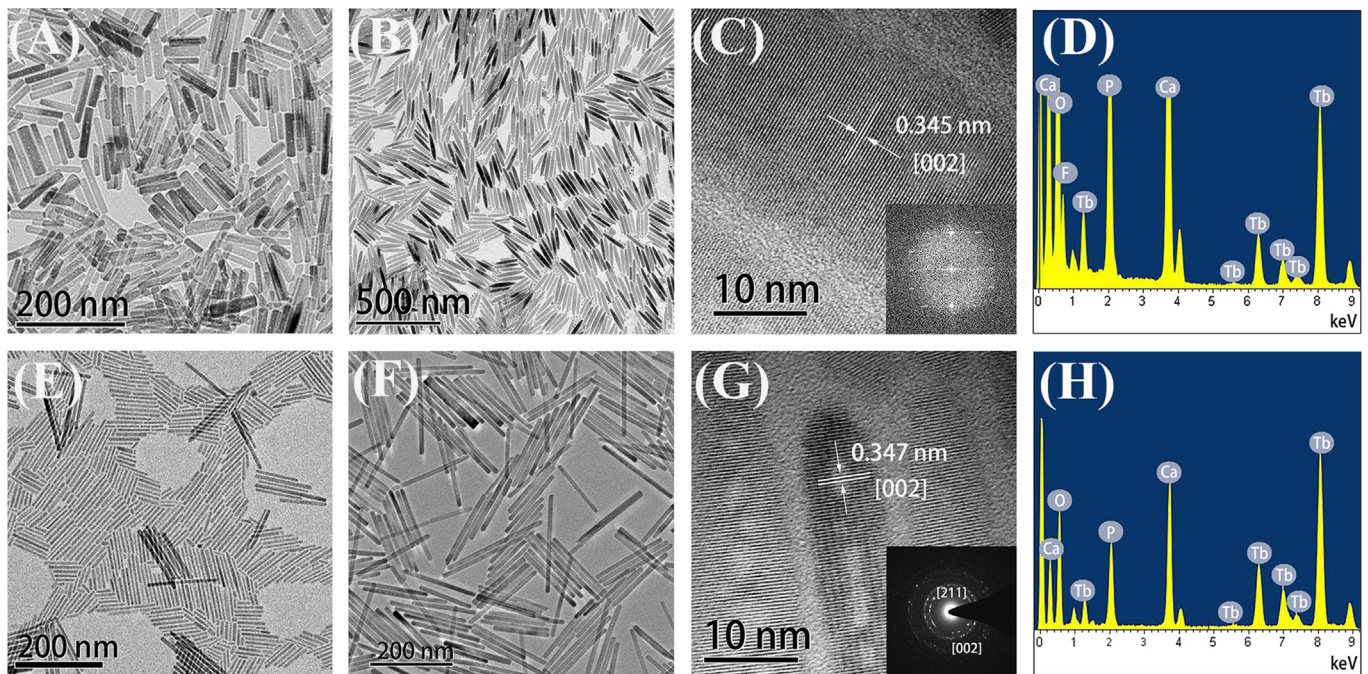
### 3. Results and discussion

It can be seen from the TEM results in [Fig. 1](#) that both FA and HA crystals are in nanoscale and show a rod-like morphology (A and E). The crystal size is about  $13 \times 75 \text{ nm}^2$  for FA and  $9 \times 80 \text{ nm}^2$  for HA. After doping with  $\text{Tb}^{3+}$  ions, the length of both apatite crystals increases remarkably, the average dimension of Tb-doped FA and HA crystals changes to about  $15 \times 140 \text{ nm}^2$  and  $12 \times 180 \text{ nm}^2$  respectively, and the shape uniformity of  $\text{FA:Tb}^{3+}$  (B) and  $\text{HA:Tb}^{3+}$  (F) crystals is better than that of FA and HA crystals. The HRTEM images (C and G) give the interplanar spacing of (002) lattice plane for  $\text{FA:Tb}^{3+}$  (0.345 nm) and  $\text{HA:Tb}^{3+}$  (0.347 nm), which is in accord with that observed in XRD patterns ([Fig. 2A](#)). The EDS element mapping (D and H) demonstrates the successful incorporation of  $\text{Tb}^{3+}$  ions in the apatite crystal structure. The results indicate that the doping of Tb ions can promote preferential growth of FA and HA crystals along the c-axis

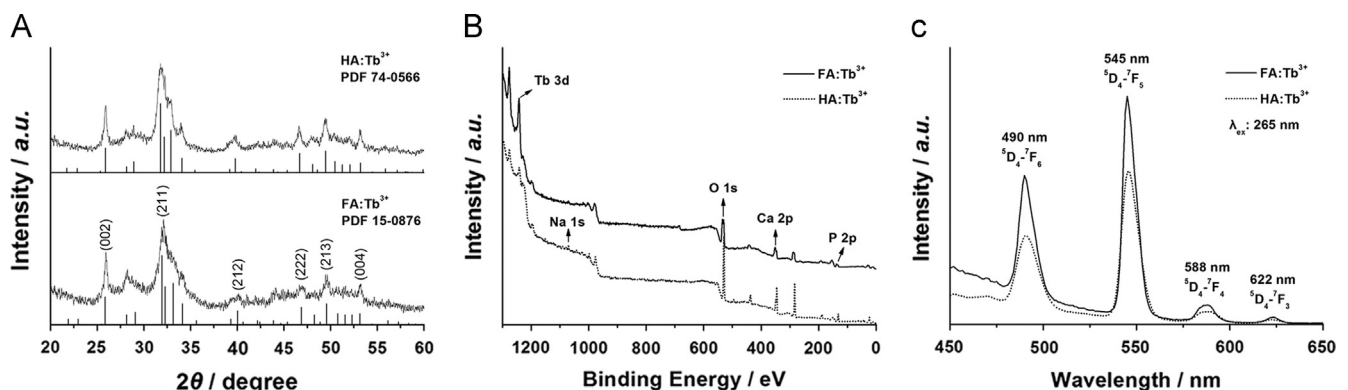
(002) direction, and the doped nanocrystals have a typical single crystal structure and uniform morphology.

The XRD patterns of both doped crystals in [Fig. 2A](#) can be indexed to the classical hexagonal phase of  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  (ICDD 15-0876) and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (ICDD 74-0566). The sharp characteristic peaks around  $25.9^\circ$  and  $31.9^\circ$  correspond to (002) and (211) lattice planes. The measured lattice parameters  $a=b=0.939 \text{ nm}$ , and  $c=0.688 \text{ nm}$  for  $\text{FA:Tb}^{3+}$ , and  $a=b=0.944 \text{ nm}$ , and  $c=0.688 \text{ nm}$  for  $\text{HA:Tb}^{3+}$  are in good agreement with the data of FA ( $a=b=0.937 \text{ nm}$ , and  $c=0.688 \text{ nm}$ ) and HA ( $a=b=0.942 \text{ nm}$ , and  $c=0.688 \text{ nm}$ ), besides the tiny increase of the  $a$ -axis. The  $a$ -axis dimension of  $\text{FA:Tb}^{3+}$  is smaller than that of HA:  $\text{Tb}^{3+}$  without change of the  $c$ -axis. The hexagonal crystal structure of apatite has good stability, which would be helpful for stable fluorescence expression of the embedded rare-earth ions.

The XPS spectra in [Fig. 2B](#) show that the peaks of Tb can be clearly observed in both Tb-doped crystals, meaning a successful incorporation of  $\text{Tb}^{3+}$  ions into the crystal lattice of FA and HA. Meanwhile, a small sodium peak (Na 1s, 1072.3 eV) is also found in the nanocrystals. The binding energy data of different ions for FA:  $\text{Tb}^{3+}$  and HA:  $\text{Tb}^{3+}$  are listed in [Table 1](#). After doping of  $\text{Tb}^{3+}$  ions



**Fig. 1.** TEM micrographs, HRTEM images, and EDS element mapping of FA (A),  $\text{FA:Tb}^{3+}$  (B–D), HA (E), and  $\text{HA:Tb}^{3+}$  (F–H) nanocrystals. The inset in (C) shows the FFT pattern of  $\text{FA:Tb}^{3+}$ , and the inset in (G) shows the SAED pattern of  $\text{HA:Tb}^{3+}$ .



**Fig. 2.** XRD patterns (A), XPS spectra (B) and emission spectra (C) of  $\text{FA:Tb}^{3+}$  and  $\text{HA:Tb}^{3+}$  nanocrystals.

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