Structural properties and self-activated photoluminescence emissions in hydroxyapatite with distinct particle shapes

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The understanding on defect-related photoluminescence (PL) properties of hydroxyapatite (HA) particles has a fundamental importance in the technological field for the development of new non-toxic biomedical and optical devices. However, the mechanisms responsible for this intrinsic PL in HA are not completely elucidated in the literature yet. In the present paper, stoichiometric and calcium-deficient HA nano- and micro-particles were synthesized by chemical precipitation. The influence of structural and morphological features on the intrinsic PL and electronic structure of this material were investigated by varying the addition rate of the phosphate precursor (0.15, 7.00 or 600.00 mL/min) and pH (4.5–5.0 or 9.5–10.0) value adopted in the precipitation. The results indicated that the structural order at long- and short-range varied with the synthesis conditions and particle shapes (rods, needles, plates, and rices). The blue and green PL emissions were attributed to defects (bulk, surface and interface) in the samples. These defects promoted the formation of additional energy levels within the band gap, as revealed by using two distinct excitation wavelengths for photoemission measurements. The energies of these wavelengths (~ 3.54 and ~ 2.98 eV at 350 and 415 nm, respectively) were lower than the band gap energies of HA samples (from 5.59 to 5.72 eV). A general model was proposed to explain the occurrence of self-activated PL in HA structure.

1. Introduction

The development of new compounds with highly efficient and tunable optical properties has become increasingly challenging for industry. In special, scientists and engineers have focused significantly on investigating and optimizing inorganic solids that consist of luminescent centers. Various optical devices, such as fluorescent lamps, light-emitting diodes, luminescent pigments, and sensors, which are based on these systems, have been obtained [1–4]. In the biomedical field, fluorescent materials, such as metal chalcogenide quantum dots, noble metal particles, lanthanide-based materials, etc, are promising candidates for bioimaging and monitored drug delivery because of their intense, stable, and tunable emissions [5–8]. However, the production of luminescent materials composed of environmentally friendly and non-toxic particles remains challenging.

In the last few decades, apatite-type materials have been used as hosts for different luminescent centers, especially transition metals and lanthanides [9,10]. In particular, hydroxyapatite (HA) is typically doped with Eu^{3+} and Tb^{3+} for biomedical approaches, owing to the luminescence properties of these lanthanide elements, and the biocompatibility, drug-loading efficacy, and cell-internalization capability of the final material [11–18]. However, intense self-activated photoluminescence (PL) processes are expected in HA samples because of the presence of high densities of structural and superficial defects arising from chemical synthesis at low temperatures [19]. Previous studies have demonstrated the application of these HA systems as fluorescent agent for bioimaging and biolabeling [20,21], monitored drug delivery systems [22,23], white-light emitting diodes [24] and so on. Although less investigated than Ln^{3+}-doped HA and other fluorescent systems, HA with self-activated PL can be technologically advantageous in terms of cost, and non-toxicity; however, the mechanisms responsible for intrinsic PL in HA are not completely elucidated in the literature.

Stoichiometric HA [SHA, $Ca_{10}(PO_4)_6(OH)_2$] is composed of phosphate clusters ($[PO_4]$), typically forming a hexagonal crystal pattern that is described by space group $P6_3/m$ [25]. Ca species occupy distinct crystallographic sites in this structure, and the corresponding general

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formula of SHA is given as $Ca(1)_4Ca(2)_6(PO_4)_6(OH)_2$. Ca(1) sites form columns on the ternary axes of the structure, which are surrounded by nine O atoms belonging to PO_4 tetrahedra, thereby resulting in $[CaO_9]$ clusters. Ca(2) sites are located at the corners of equilateral triangles and hence, form the hexagonal channels of the structure. These species are surrounded by six O atoms that comprise the $[PO_4]$ clusters and one OH group inside the channel, thereby leading to $[CaO_7H]$ clusters. The hexagonal character of the HA lattice can be retained, even in the presence of various ionic substitutions and vacancies [26–28]. This feature is also evidenced by the fact that HA exists in the non-stoichiometric, Ca-deficient form, which is typically represented as $Ca_{10−x}(HPO_4)_x(PO_4)_{6−x}(OH)_{2−x}$ $(0 < x < 1)$(Ca-dHA) [29]. Ca-dHA has distinct chemical properties compared to SHA; for example, its higher solubility leads to an increase in the bioresorption rate in vivo [30]. Moreover, vacancies in Ca-dHA lead to changes in the electronic structure and density of $e'–h^•$ pairs [31] which, in turn, may affect the intrinsic PL emission.

Various mechanisms have been proposed in order to explain the intrinsic PL of HA [21,32,33]. However, the effect of the degree of structural order-disorder, chemical composition, and morphological features, on the self-activated PL and electronic structure of HA particles, remains unclear. Moreover, several synthesis methods have been employed to obtain HA [34]. One of these methods, chemical precipitation, can be used to obtain distinct particle shapes and introduce several types of defects into the structure, in order to understand its PL. Recently, our research group reported the effect of different heat treatment temperatures on the intrinsic PL of HA nanorods [35]. In the present study, SHA and Ca-dHA with distinct sizes and shapes were synthesized via chemical precipitation. The influence of pH and addition rate of phosphate precursor on the structural ordering (long- and short-range), morphological features, and PL properties of these materials were investigated in detail.

2. Experimental section

2.1. Materials and methodology

Calcium nitrate tetrahydrate $[Ca(NO_3)_2·4H_2O]$ (99%, Sigma-Aldrich) and di-ammonium phosphate $[(NH_4)_2HPO_4]$ (98 + %, Strem Chemicals) were used as starting precursors. The pH of the solutions was controlled by adding ammonium hydroxide $[NH_4OH]$ (ACS, Acros). *Milli-Q* water was used as the solvent. Two main groups were synthesized via chemical precipitation in a: (1) basic environment with addition of NH_4OH (pH_{final} = 9.5–10.0), and (2) acidic environment without addition of NH_4OH (pH_{final} = 4.5–5.0). Moreover, in order to obtain distinct particle shapes, the addition rate of the phosphate precursor in aqueous solutions containing Ca^{2+} ions, was varied. Table 1 lists the main experimental parameters. The samples were all synthesized at 90 °C.

Table 1
Experimental parameters employed in the chemical precipitation of HA.

Sample group	Sample label	Mixture method	Addition rate of phosphate precursor (mL/min)	pH_{final}
With addition of NH_4OH	BIP	Injection pump	0.15 (Slow)	9.5–10.0
	BPP	Peristaltic pump	7.00 (Moderate)	9.5–10.0
	BOB	One batch	600.00 (Rapid)	9.5–10.0
Without addition of NH_4OH	AIP	Injection pump	0.15 (Slow)	4.5–5.0
	APP	Peristaltic pump	7.00 (Moderate)	4.5–5.0
	AOB	One batch	600.00 (Fast)	4.5–5.0

2.2. Synthesis using injection pump

In this step, well-crystallized particles were obtained by slowly mixing the precursors using an injection pump. Firstly, 50 mL of an aqueous solution containing 1.0 mmol of Ca^{2+} ions, and 12 mL of an aqueous solution containing 0.6 mmol of the phosphate precursor were prepared; these were referred to as solution 1 and solution 2, respectively. In order to obtain the sample prepared in a basic environment, the pH of both solutions was adjusted to 9.5–10.0 by adding NH_4OH. The samples were prepared by adding solution 2 to solution 1, at an approximate addition rate of 0.15 mL/min. The mixture was then ripened for 2 h. The milky suspensions obtained were repeatedly washed with *Milli-Q* water and ethanol, and centrifuged (8000 rpm) in order to eliminate residual groups. The resulting powders were dried at 80 °C for 24 h under air atmosphere. The samples prepared with and without addition of NH_4OH were referred to as BIP (Basic – Injection Pump) and AIP (Acid – Injection Pump), respectively.

2.3. Synthesis using peristaltic pump

This synthetic route was based on our previous study published [35]. The experimental procedure was similar to that used for the synthesis via IP; however, the solutions were mixed at a moderate addition rate (7 mL/min) of phosphate precursor by using a peristaltic pump. Moreover, solutions 1 and 2 consist of 50 mL of aqueous solution containing 10 mmol of Ca^{2+} ions and 100 mL of aqueous solution containing 6 mmol of the phosphate precursor, respectively. The as-prepared samples were referred to as BPP (Basic – Peristaltic Pump) and APP (Acid – Peristaltic Pump).

2.4. Synthesis by one-batch step

This procedure was used to obtain poorly crystallized samples. The experimental parameters were similar to those described by the PP. The only difference adopted was the mixture of both solutions, which was performed by one-batch step; the addition rate of the precursor was ∼ 600 mL/min. The as-prepared samples were referred to as BOB (Basic – One Batch) and AOP (Acid – One Batch).

2.5. Characterization

The chemical composition of the prepared samples was determined via inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Thermo Scientific iCAP 6500 (USA) analyzer. The samples were structurally characterized by X-ray diffraction (XRD) in a Shimadzu XRD–6000 (Japan) diffractometer using *Cu-Kα* radiation (λ = 0.154184 nm). Data were collected over 2θ ranging from 20° to 70°, and at a step scan rate and step size of 0.2°/min and 0.02°, respectively. The peak broadening of the reflection was used to determine the crystallographic domain size (*Xs*) of the samples, from the Scherrer equation [36]:

$$X_S = \frac{0.9 \times \lambda}{\beta \times \cos\theta} \tag{1}$$

where λ is the wavelength of the x-rays and θ is the Bragg angle of the analyzed peak; β is the line broadening and is estimated from:

$$\beta = \sqrt{\beta_{observed}^2 - \beta_{instrumental}^2} \tag{2}$$

where $\beta_{observed}$ is the observed broadening, as determined from the full width at half maximum (FWHM), and $\beta_{instrumental}$ is the instrumental broadening, as determined from FWHM of a well-crystallized SiO_2 (quartz) external standard. In HA samples, *Xs* along perpendicular directions can be estimated by using the (002) and (300) diffraction peaks; this estimation is based on the assumption that the typical crystal growth (i.e., along *c* planes) occurs and the length of the crystal