Preparation and Characterization of Hydroxyapatite Doped with La^{3+}

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Statement of Purpose: Hydroxyapatite (HA) is the main mineral composition of natural bone. Addition of traces of ions to HA may affect the dissolution rate, mechanical properties and biological properties of HA. Rare earth element, such as lanthanum (La), has attracted much attention in recent years. It was reported that bone-forming cells, adhered and differentiated at earlier time points in response to the La^{3+}-doped HA than HA doped with divalent cations. Moreover, the HA doped with La^{3+} shows superior mechanical properties and thermostability. The aims of the study were to investigate the effect of La^{3+} doping on the HA property change. It is expected that the La^{3+} doped HA will have great potential to be used in orthopedic and dental applications.

Methods: Hydroxyapatite particles was prepared using a wet synthesis method. Briefly, 0.16 M of $(NH_4)_2HPO_4$ solution was dropped into 0.45 M $Ca(NO_3)_2{\cdot}4H_2O$ solution (0.45 M, pH~11) at a Ca/P ratio of 1.67. After reaction, the solution was stirred at 95°C for 5 h, followed by washing and drying at room temperature. La^{3+} was incorporated using an ion-exchange method as follows (La-HA): 1 g of the as-prepared HA particles were dispersed in 200 ml 0.1-0.5 M $LaCl_3$ solution for 0.5 h, then the pH of the solution was adjusted to 7 by adding $NH_3{\cdot}H_2O$. In 30 min, the process was repeated for 3 times.

The molecular ratio of La/Ca was analyzed using energy dispersive X-ray analysis attached to a field emission scanning electron microscope (FESEM). The surface morphology and phase of HA and La-HA were characterized using transmission electron microscopy (TEM) and X-ray diffraction (XRD), respectively. The peak position and the full width half maximum of the peak were calculated using PEAKFIT software. Fourier transformed infrared (FTIR) spectrometry was also used to examine HA and La-HA powders.

Results: The La-HA particles were elongated after the ion exchange process (Figure 1). Their average aspect ratio was 3-6 times of that of HA.

In the XRD pattern of HA and La-HA (Figure 2), the main phase of La-HA was attributed to HA. However, $LaPO_4$ was also detectedas the solubility of $LaPO_4$ is lower than that of HA. Consequently, in the presence of La^{3+} ions, $LaPO_4$ was precipitated during the ion exchange in the solution. A shift of 0.01° ~0.03° to the lower degree of (002) peak of HA was observed in the case of La-HA, indicating La^{3+} was incorporated into the HA lattice, resulting inthe expansion of lattice c. Based on the results calculated by PEAKFIT software, the (002) peak at ~25.8° became wider when more La^{3+} were incorporated into HA. Therefore, the average crystal size of La-HA was smaller than HA. Probably, the HA was dissolved slightly during the ion exchange process.

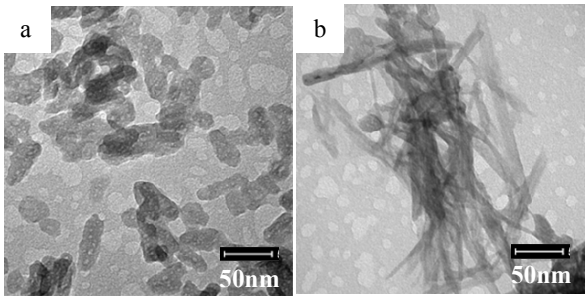

Figure 1. TEM XRD (a) HA, (b) La-HA: La/Ca=0.31

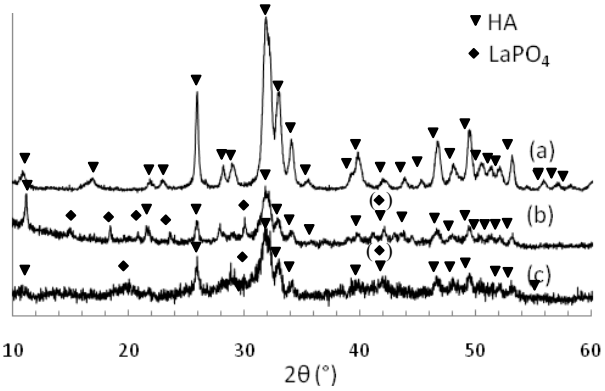

Figure 2. XRD of (a) HA, (b) La-HA: La/Ca=0.31, (c) La-HA: La/Ca=0.42.

In FTIR spectra (Figure 3), the absorption peaks at 1440-1600 cm^{-1} denoted the stretching mode of the CO_3^{2}, which was much higher in the La-HA comparing to pure HA, indicating more CO_3^{2-} had incorporated into La-HA. The carbonate groups partially replaced the $(PO_4)^{3-}$ groups in HA, which is B-type substitution. Carbonate could result in the distortion of the crystallographic lattice of HA, leading to the contraction in a-axis and extension in c-axis. This also explains why La-HA exhibits a higher aspect ratio (Figure 1).c

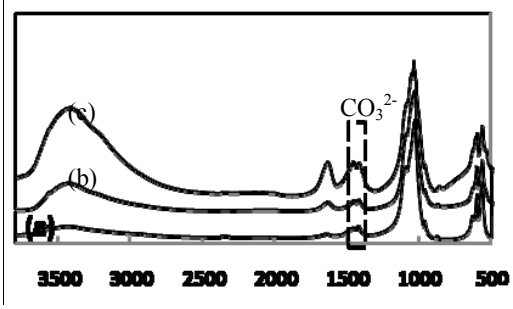

Figure 3. FTIR patterns of (a) HA;(b) La-HA: La/Ca=0.13 (c) La-HA: La/Ca=0.41

Conclusions: La^{3+} can partially replace Ca^{2+} in HA and form into La-HA which exhibits an elongated structure, although some $LaPO_4$ precipitated simultaneously. The elongation of La-HA is due to the uptake of CO_3^{2-} during the ion exchange process.