

Preparation and characterization of nano-sized hydroxyapatite particles and hydroxyapatite/chitosan nano-composite for use in biomedical materials

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Abstract

Natural bone is actually an inorganic/organic composite mainly made up of nano-structure hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAp) and collagen fibers. It is of most importance to synthesize nano-composites of inorganic/organic in order to have good biocompatibility, high bioactivity and great bonding properties. In this work, HAp nano-particle and HAp/chitosan (CTS) nano-composite with a homogeneous microstructure were prepared and characterized. It is proposed that the nano-structure of hydroxyapatite/chitosan composite will have the best biomedical properties in the biomaterials applications.

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1. Introduction

Hydroxyapatite (HAp), a major inorganic component of bone, has been used extensively for biomedical implant applications and bone regeneration due to its bioactive, biodegradable and osteoconductive properties [1–3]. However, the application of pure HAp is very limited due to its brittleness. Since the natural bone is a composite mainly consisted of nano-sized, needle-like HAp crystals and collagen fibers, many efforts have been made to modify HAp by polymers, such as polylactic acid [4,5], collagen [6], chitosan [7],

polyethylene [8,9]. Among these polymers, the biopolymers have received much attention in the field of medical applications, due to their excellent biocompatibility and biodegradability. Chitosan (CTS), a kind of polysaccharide and natural polymer, is the partially deacetylated form of chitin that can be extracted from crustacea. It degrades in the body to non-harmful and non-toxic compounds and has been used in various fields such as nutrition, metal recovery and biomaterials [7,10]. HAp/CTS composite combines their advantages and has gained much attention from biologists and biomaterial scientists. In this work, HAp nano-particle, HAp/CTS nano-composite with a homogeneous microstructure were prepared.

Hydroxyapatite was synthesized in aqueous solutions according to the method proposed in Ref. [11].

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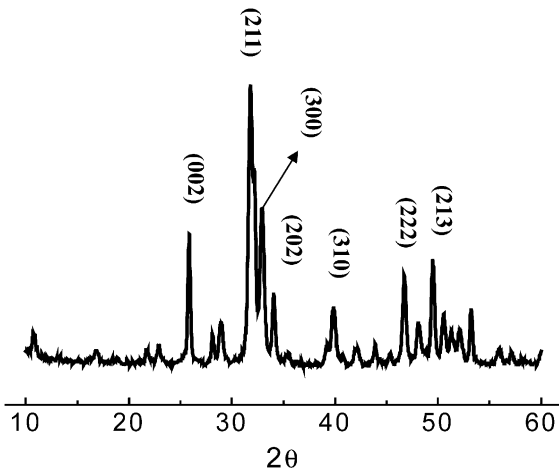


Fig. 1. XRD spectra of HAp nanoparticles.

The pH values of the solutions of $\text{Ca}(\text{NO}_3)_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$ were adjusted at more than 10 with ammonia. Then they were mixed with a stoichiometric ratio of Ca to P (= 1.67). After the reaction was finished, the precipitate was rinsed for several times with distilled water until the pH value decreased to 7. In order to avoid serious aggregation of the ultrafine powder during drying, the water in the precipitate was replaced by *n*-butanol. Then the precipitate was dried at about 80 °C and calcined at 400 °C to get rid of the rudimental organic compound.

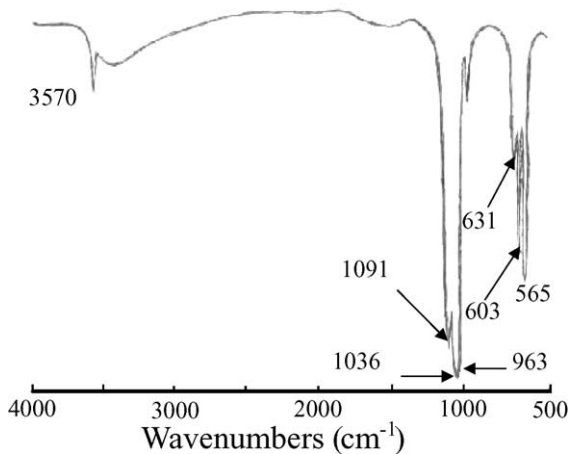


Fig. 2. IR spectra of HAp nanoparticles.

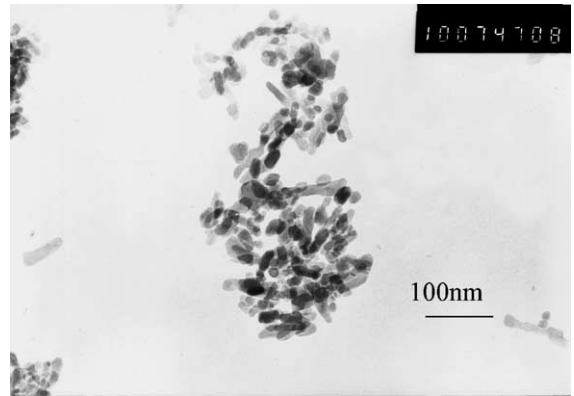


Fig. 3. TEM photograph of HAp nanoparticles.

The HAp/CTS nano-composite was prepared also by precipitation method. The aqueous solution of $\text{NH}_4\text{H}_2\text{PO}_4$ was added to the mixture of the aqueous solution of $\text{Ca}(\text{NO}_3)_2$ and CTS whose degree of deacetylation is 84%. Then the precipitate was treated by the same procedure as mentioned above, rinsed with distilled water and observed directly.

For characterizing the crystal phases for HAp/CTS nano-composite, X-ray diffractometer (XRD, Rigaku Rotaflex D/max-C) and Infrared Spectrophotometry (IR, Nicolet AVATAR FT-IR 360) were performed on the powder. The particles were observed by a JEM-100CX II transmission electron microscopy. The spe-

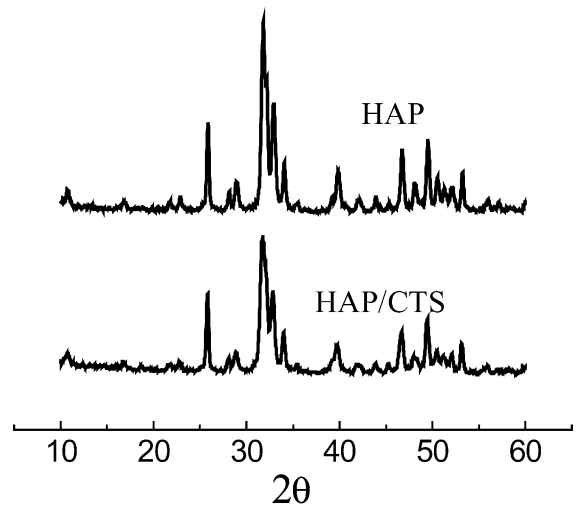


Fig. 4. XRD spectrum of as-prepared HAp nanoparticles and HAp/CTS composite.

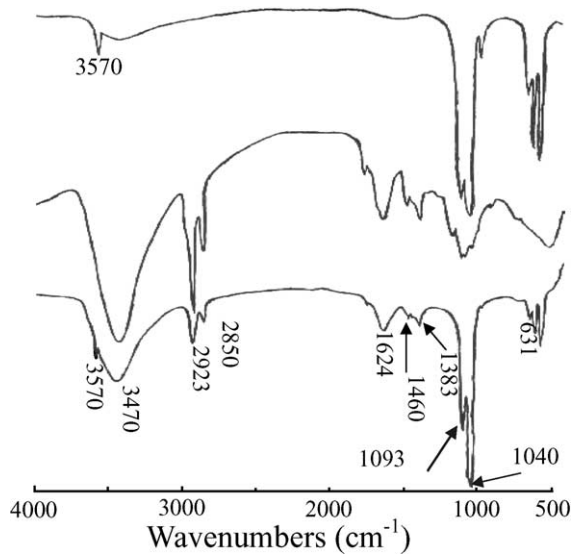


Fig. 5. IR spectrum of HAp, CTS and HAp/CTS composite.

cific surface area of the HAp particles was measured by the BET method (SORPTOMATIC 1900) on powder degassed at 300 °C.

The XRD and IR spectra of nano-HAp powder are depicted in Figs. 1 and 2. The XRD pattern was verified by the Powder Diffraction File (PDF Card No. 9-432). Due to the ultrafine nature of the powder, there is an extensive degree of peak broadening in the X-ray diffraction pattern. As shown in IR spectra (Fig. 2), the two bands at 631 and 3570 cm^{-1} belong to the vibration of hydroxyl. Those bands at 1036, 1091 and 963 cm^{-1} are the characteristic bands of phosphate stretching vibration, while the bands at 603 and 565 cm^{-1} are due to phosphate bending vibration. From these measurements, the precipitate particle is proved to be hydroxyapatite.

The TEM micrograph of HAp powder is shown in Fig. 3. The powder exhibits no serious aggregation. The size of the particles is about 20–30 nm in width and 50–60 nm in length. The specific surface area of the powder is 73.0 m^2/g . In this work, organic solvent,

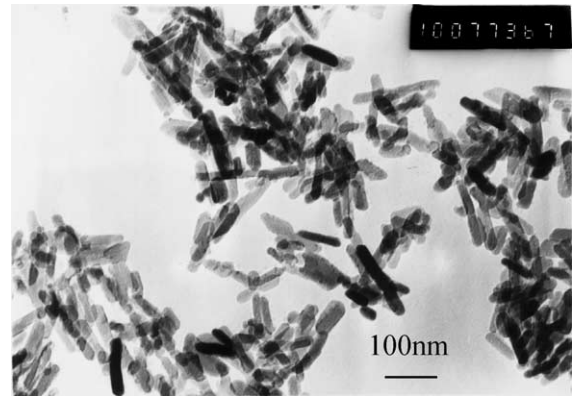


Fig. 6. TEM micrograph of HAp/CTS composite.

n-butanol, was used to replace the water in the system because it can decrease the two major factors that cause the agglomeration of nano-powder when drying from aqueous solutions: one is the capillary pressure between the adjacent particles due to the evaporation of water and the other is the hydrogen bond originating from the water molecules on the surface of adjacent particles.

Fig. 4 indicates the results of XRD measurements on the prepared nano-HAp and HAp/CTS nano-composite. HAp peaks are observed in the composite and line-broadening phenomena are also demonstrated in the spectra.

The IR spectrum of the nano-sized HAp, CTS and HAp/CTS composite are presented in Fig. 5. The composite is characterized by absorption bands arising from HAp and CTS, determined by analogy with IR spectrum of HAp and CTS standard samples. As mentioned above, the bands at 3570, 631 and 1000–1100 cm^{-1} are attributed to the hydroxyl and phosphate groups of HAp. The vibration of the OH, NH, CH and C=O groups of CTS in the HAp/CTS composite is shown in Table 1.

Fig. 6 shows the TEM micrograph for the nano-sized composites. The particles retain the ultrafine nature and disperse well in water. The composite is of

Table 1

The vibration bands of groups from the CTS in HAp/CTS composite

Groups	O–H	N–H	C–H	C=O	C–O
Bands (cm^{-1})	~ 3470	Included in ~ 3470 1624	2923, 2850, 1460, 1383	Included in 1624	Overlapped with the bands of phosphate (1150–1040)

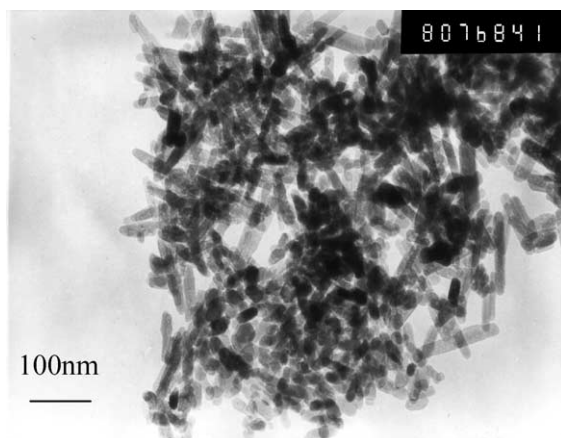


Fig. 7. Some HAp nanoparticles at the edge of HAp/CTS cluster prepared by mixing HAp/CTS mixture and NaOH solution.

an almost homogeneous microstructure and keeps deflocculation property that allows better quality control. This advantage may be helpful for forming uniform block materials, especially when using colloidal processing along with slip casting.

There were some reports concerning other methods to prepare regular sized HAp/CTS composite. Ito et al. [12] dispersed the HAP grains in the acid solution of CTS to prepare HAp/CTS composite membrane or paste. According to the insolubility of HAP and CTS in strong basic medium, mixing the HAp/CTS mixture and KOH (or NaOH) solution with pH more than 12 was another method to obtain HAp/CTS composite [7]. The instantaneous precipitation of CTS forms enclosed HAP particles inside polymer fibers. The nano-sized HAp/CTS composite was prepared by this method in the work. With the adding of NaOH solution, flocculent precipitate formed quickly, which was very unstable and settled to the bottom of the container fast. The TEM micrographs show that the composite consists of clusters. And some HAP nano-particles can be discerned at

the edge of the clusters (Fig. 7). Obviously, the uniformity of this composite is not as good as that prepared by precipitation method.

In conclusion, nano-sized hydroxyapatite powder was synthesized successfully in aqueous solutions. The particle size is about 20–30 nm in width and 50–60 nm in length. The specific surface area of the powder is 73.0 m²/g. Using this nano-powder, hydroxyapatite/chitosan nano-composites are also prepared by the precipitation. The particles are of an almost homogeneous microstructure that will be helpful to produce uniform nano-material. It is proposed that the nano-structure of hydroxyapatite/chitosan composite will have the best biomedical properties in the biomaterials applications.

Acknowledgements

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