SURFACE STRUCTURE AND PROPERTIES OF CALCIUM HYDROXYAPATITE PARTICLES MODIFIED WITH PYROPHOSPHORIC ACID

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Abstract Synthetic colloidal calcium hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$: Hap) was treated with pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$: PP) in acetone and the materials were characterized by a variety of techniques. XRD pattern and morphology of Hap particles were essentially not changed by the modification. The additional amount of PO_4 of Hap increased with an increase of PP concentration and the Ca/P molar ratio of the particles decreased from 1.62 to 0.81. IR results indicated that the isolated surface P-OH band developed with increasing the PP concentration up to 6.0 mmol dm^{-3} by the reaction of isolated surface P-OH groups of Hap and PP. Above $10.2 \text{ mmol dm}^{-3}$, hydrogen-bonding surface P-OH band appeared at 2913 cm^{-1} and enlarged with increasing the PP concentration, while the isolated surface P-OH band weakened. The results of N_2 and H_2O adsorption measurement revealed that the modified particles rather aggregated compared to the unmodified ones.

INTRODUCTION

Calcium hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ designated as Hap, is a principal component of hard tissues and has been of interest in industry and medical and dental fields. Synthetic colloidal Hap particles find many applications such as adsorbents for chromatography to separate protein and enzyme, catalysts for dehydration and dehydrogenation of alcohols, methane oxidation, and artificial teeth and bones.¹⁻⁶ These properties relate to various surface properties of Hap, *e.g.*, surface functional groups, acidity and basicity, surface charge, hydrophilicity and porosity. It has been found that the Hap surface possesses ca. $2.6 \text{ groups nm}^{-2}$ of P-OH groups acting as the adsorption sites for CO_2 , CH_3OH , H_2O , *n*-butylamine and acetic acid.⁷⁻¹¹ Hence, the regulation of number and kinds of surface P-OH groups is expected to change the aforementioned properties of Hap. However, to our knowledge, no study has been reported on regulation of surface P-OH groups.

The aim of this study was to alter the surface structure and properties of Hap particles by modifying with PP. Therefore, the synthetic colloidal Hap particles were treated with various PP concentrations and the surface nature of the materials were investigated by FTIR, molecular adsorption, XRD, TEM, elemental analysis and so on.

EXPERIMENTAL

The colloidal Hap particles were synthesized from a wet method by aging the precipitates formed from the reaction of $\text{Ca}(\text{OH})_2$ solutions with H_3PO_4 in a sealed Teflon vessel under CO_2 -free conditions at 100°C for 48 h. The Ca/P molar ratio of Hap thus prepared was 1.62, meaning that the material was Ca^{2+} -deficient.

Surface modification of Hap was carried out as follows. One gram of the synthetic Hap particles dried at 140°C for 24 h in an air oven was treated by refluxing in 60 ml of 0 - $76.8 \text{ mmol dm}^{-3}$ PP acetone solution at the boiling temperature of the solution for 5 h. The PP-treated particles were filtered off, thoroughly washed with acetone, and finally dried in an air oven at 50°C for 24 h. All the chemicals were reagent grade and were used without further purification.

The materials thus obtained were characterized by various techniques. Powder X-ray diffraction (XRD) patterns were taken on a Rigaku diffractometer with a Ni-filtered $\text{CuK}\alpha$ radiation. Particle morphology was observed by a JEOL transmission electron microscope (TEM). Ca and P contents were assayed by a Perkin-Elmer atomic absorption spectrometer (AAS) and a molybdenum blue method, respectively, after dissolving the sample in HCl solution. Specific surface area was estimated from the N_2 adsorption isotherms measured by a Quantumchrome volumetric apparatus at the boiling temperature of liquid nitrogen fitting the BET equation. Adsorption isotherms of H_2O were determined by a gravimetric technique at 25.0°C . Transmission IR spectra *in vacuo* at room temperature were recorded by a self-supporting disk method using a JASCO Fourier transform infrared (FTIR) spectrometer. Before the molecular adsorption and IR measurement, the samples were evacuated at 300°C for 2 h.

RESULTS AND DISCUSSION

Structure of Modified Hap

The XRD patterns of the modified Hap showed only the peaks due to Hap and no pronounced change on crystallinity was recognized. By the TEM observation, the unmodified particles were rod-shaped and their mean sizes were ca. 70 nm (length) and ca. 17 nm (width). The particle morphology and sizes were essentially unchanged by the treatment and no new particles were generated. Figure 1 shows the change of Ca/P molar ratio

FIGURE 1 Plots of molar ratio Ca/P and additional amount of PO_4 of Hap against [PP].

of the modified Hap against PP concentration. Hereafter, PP concentration is abbreviated as [PP]. The molar ratio Ca/P decreases with increasing [PP]. This seems to be due to the increment of PO₄ content in the materials, because the dissolution of Hap particles was not confirmed during the treatment. These facts reveal that PP reacts with the particle surface of Hap. To know the modification extent, the additional amount of PO₄ on the modified materials was estimated from Ca and P contents and was also shown in Fig. 1. Clearly seen, the additional amount of PO₄ increases with raising [PP]. The details of modification process will be described later.

Surface Structure of Modified Hap

In order to explore the surface structure of the modified Hap, IR spectra were taken. Figure 2 shows the IR spectra *in vacuo* at room temperature of Hap unmodified and modified with different [PP]. Before the measurement, the samples were outgassed at 300°C for 2 h. Spectrum of the unmodified Hap possesses a strong absorption band at 3570 cm⁻¹ and a weak one at 3660 cm⁻¹. The former band is due to the OH⁻ ions in the Hap lattice and the latter one to the O-H stretching vibration mode of isolated surface P-OH groups generated by the protonation of surface PO₄³⁻ ions to maintain the charge balance of Hap particles.^{7,8} In spectrum of the Hap modified at [PP] = 2.0 mmol dm⁻³, a new band founds at 3670 cm⁻¹. By H-D isotope exchange, this band can be ascribed to the O-H stretching vibration modes of additional isolated surface P-OH groups formed by the reaction of surface P-OH groups of Hap and PP as follow:

Besides, the additional surface P-OH groups formed also react with PP as follow :

Note that the number of surface P-OH groups formed by the reactions (1) and (2) corresponds to additional amount of PO₄ of the materials, meaning that the number of surface P-OH groups of Hap increases with increasing the additional amount of PO₄. When the materials are modified at [PP] ≤ 6.0 mmol dm⁻³, the isolated surface P-OH band develops with an increase of [PP]. Interestingly, this band steeply weakens at [PP] = 6.0 mmol dm⁻³. Furthermore, a new broad band centered at 2913 cm⁻¹

FIGURE 2 IR spectra *in vacuo* of Hap modified with various [PP]. [PP] (mmol dm⁻³): (a) 0, (b) 2.0, (c) 6.0, (d) 10.2, (e) 17.3, (f) 33.7, (g) 52.6, (h) 76.8.

appears at $[PP] = 10.2 \text{ mmol dm}^{-3}$ and the band enlarges on raising $[PP]$. To get further insight into these bands, Figure 3 plots the area intensity of isolated surface P-OH and 2913 cm^{-1} bands as a function of $[PP]$. On modifying at $[PP] \leq 6.0 \text{ mmol dm}^{-1}$, the area intensity of isolated surface P-OH band steeply rises with increasing $[PP]$. Modifying at $[PP] = 10.2 \text{ mmol dm}^{-3}$ increases the intensity of 2913 cm^{-1} band and suddenly reduces the intensity of isolated surface P-OH band. At $[PP] \geq 10.2 \text{ mmol dm}^{-3}$, the 2913 cm^{-1} band further intensifies,

FIGURE 3. Plots of area intensities of isolated surface P-OH and 2913 cm^{-1} bands vs. $[PP]$.

while the isolated surface P-OH band slightly decreases. The foregoing results imply that the state of surface P-OH groups is altered at $[PP] \geq 10.2 \text{ mmol dm}^{-3}$. To assign the 2913 cm^{-1} band, H-D exchange of unmodified and modified materials was examined by IR spectroscopy. For the unmodified Hap, the isolated surface P-OH band weakened with the H-D exchange and the isolated surface P-OD and OD⁻ bands were found at 2702 and 2630 cm^{-1} , respectively (not shown here). In case of Hap modified at $[PP] = 52.6 \text{ mmol dm}^{-3}$, the isolated surface P-OH band slightly weakened with H-D exchange and the isolated surface P-OD band at 2710 cm^{-1} and OD⁻ band at 2630 cm^{-1} appeared as well as the unmodified Hap. Besides these bands, a broad band at 2913 cm^{-1} weakened and a new broad band developed at 2160 cm^{-1} . The wavenumber ratio of 2913 and 2160 cm^{-1} bands is 1.349 , close to $1.354 - 1.355$ of the isolated surface P-OH/P-OD ($3660/2702$, $3670/2710$) and lattice OH⁻/OD⁻ ($3570/2630$) detected on unmodified and modified Hap and 1.374 of the theoretical ν_{OH}/ν_{OD} ratio. These facts allow us to infer that a broad band centered at 2913 cm^{-1} is assigned to the surface P-OH groups. Low and Ramamurthy indicated by IR measurement of phosphoric acid impregnated silica gel that a broad band at ca. 3000 cm^{-1} is due to the hydrogen-bonding surface P-OH groups.¹² The position of the 2913 cm^{-1} band detected in the present study almost corresponds to that of ca. 3000 cm^{-1} band of surface hydrogen-bonding P-OH groups. From these results, the broad 2913 cm^{-1} band observed in Fig. 2 can be assigned to the hydrogen-bonding surface P-OH groups. The formation of the 2913 cm^{-1} band can be explained by considering that the number and density of surface P-OH groups of Hap increase after modifying with $[PP] \geq 10.2 \text{ mmol dm}^{-3}$, resulting in the adjacent additional hydrogen-bonding surface P-OH groups.

Adsorption of N₂ and H₂O

We measured the adsorption isotherms of N₂ on unmodified and modified Hap. Before the adsorption, the samples were outgassed at 300°C for 2 h. All the isotherms belonged to type II in the IUPAC classification. The amount of N₂ adsorbed gradually decreased with increasing [PP]. Figure 4 plots the specific surface area (SN₂) estimated from the N₂ adsorption isotherms fitting the BET equation against [PP]. The SN₂ monotonously decreases on raising [PP]. As indicated above, the surface hydrogen-bonding P-OH groups are formed on Hap at [PP] ≥ 10.2 mmol dm⁻³. It can be, therefore, inferred that the hydrogen-bond of P-OH groups is generated not only on primary Hap particles but also among the aggregated particles. As a result, the modified Hap particles seem to more aggregate than the unmodified ones, leading to the reduction in effective surface area available for N₂ adsorption.

To confirm this, the H₂O adsorption isotherms on unmodified and modified Hap were measured and monolayer adsorption capacity of H₂O molecules per unit surface area obtained by N₂ adsorption (n_w) is plotted against [PP] in Fig. 4. The n_w of the materials modified at [PP] ≤ 6.0 mmol dm⁻³ is close to 9.3 molecules nm⁻² of theoretical n_w , estimated using 0.108 nm² as the cross-sectional area of a H₂O molecule, depicted by a dotted line in this Figure. The n_w steeply rises to ca. 25 molecules nm⁻² at [PP] = 10.3 - 33.7 mmol dm⁻³ and then slightly increases. These facts strongly indicate that the modified particles rather aggregate compared to the unmodified ones and that the ultramicropores form among the particles which can accept H₂O molecules but not N₂ molecules.

FIGURE 4. Plots of specific surface area (SN₂) and monolayer adsorption capacity of H₂O molecules (n_w) for the modified Hap vs. [PP].

CONCLUSIONS

The results obtained in this study can be summarized as follows. The PP molecules react with surface P-OH groups of Hap to yield additional surface P-OH groups. Raising the [PP] increases the additional amount of PO₄ and number of surface P-OH groups of Hap. The particle morphology was essentially not altered during the modification. At [PP] ≤ 6.0 mmol dm⁻³, the isolated surface P-OH band of Hap

developed with an increase of [PP]. The hydrogen-bonding surface P-OH band appeared at $[PP] \geq 10.2 \text{ mmol dm}^{-3}$ and was intensified by increase in the [PP]. While the isolated surface P-OH band was weakened. The modified Hap particles rather aggregate than the unmodified ones. This fact explained by the formation of hydrogen-bonding surface P-OH groups among the particles. This was further supported by N_2 and H_2O adsorption measurement.

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