SURFACE MODIFICATION OF CALCIUM HYDROXYAPATITE WITH 3-AMINOPROPYLTRIETHOXYSILANE

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Abstract The surface of synthetic calcium hydroxyapatite (Hap) particles was modified with 3-aminopropyltriethoxysilane (APS: NH(CH₃)₃Si(OC₂H₅)₃) in 95% ethanol solutions and the resulting materials were characterized by various means. No remarkable change in XRD pattern, molar ratio Ca/P, specific surface area and particle morphology of the Hap was recognized by the modification. The number of surface aminopropyl group of Hap increased from 0 to 4.2 molecules nm⁻² as the APS concentration increases. IR results indicated that APS reacted with surface P-OH groups of Hap and formed -Si-OH groups.

INTRODUCTION

Calcium hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂: Hap) is a major component of hard tissues in animal organism and has been of interest in industry and medical and dental fields. Synthetic colloidal Hap particles find many applications for adsorbents of protein, catalysts for dehydration and dehydrogenation of alcohols, and artificial teeth and bones.¹-⁴ These properties relate to the surface nature of Hap, e.g., surface functional groups, acidity and basicity, surface charge, hydrophilicity and porosity. It has been found that Hap surface possesses P-OH groups acting as an adsorption site for CO₂, CH₃OH, H₂O, n-butylamine and acetic acid.⁵-¹⁰ Hence, the regulation of surface P-OH groups is expected to change the aforementioned properties of Hap. Thus, the modification of Hap surface is anticipated to give novel functions to this material. Previously, we reported the surface modification of Hap with alkyl phosphates¹¹-¹³, hexanoic and decanoic acids¹⁴ for the purpose of using this material as a filler of cements and polymers, and adsorbent for proteins and indicated that the hydrophilic Hap surface turns into hydrophobic by the modification.

In industry, to alter surface structure and property of metal oxide particles such as SiO₂, Al₂O₃ and TiO₂, these materials were treated by silane coupling agent with various functional groups e.g., alkyl, thiol, amino and so on. Hence, the treatment of Hap with silane coupling agent may alter the surface structure of this material. Furuzone et al.¹⁵ reported that the Hap modified with γ-aminopropyl trimethoxysilane...
was coupled to acrylic acid grafted silicon sheet by covalent linkage of amide-bond (-CONH-). Although, this study was not fully elucidated the surface modification mechanism of Hap. To corroborate the interaction between amino- modified Hap and carboxylic acid, particularly to carboxylic group, is of great interest in dental and medical fields concerned with biomineralization because animal organisms contain various kinds of carboxylic acids existing in proteins, lipids, vitamins and metabolic inhibitors including acetic, pyruvic and citric acids. Further, introducing the amino groups on Hap surface alter the aforementioned surface properties.

The aim of this study was to introduce amino groups on Hap surface using 3-aminopropyltriethoxysilane (NH₂(CH₂)₃Si(OC₂H₅)₃: APS) and to clarify the surface modification mechanism of Hap with APS. The synthetic Hap particles were treated with APS and the materials were characterized by FTIR, XRD, TEM and TG-DTA. The surface modification mechanism was discussed on the basis of results obtained.

EXPERIMENTAL

A synthetic colloidal Hap particle was prepared by the same wet method as described previously. The Ca/P molar ratio of Hap prepared was 1.62 less than 1.67 of stoichiometric Hap, meaning that the material is Ca-deficient.

Surface modification of Hap was carried out as follows. 0.5 grams of the synthetic Hap particles dried at 140°C for 24 h in an air oven were treated in 40 ml of 0 – 0.50 mol dm⁻³ APS 95% ethanol solution at 30°C for 5 h. The particles treated were filtered off, fully washed with ethanol and finally dried by outgassing at 150°C for 2 h.

The materials thus treated were characterized by a variety of techniques. Powder X-ray diffraction (XRD) patterns were taken on a Rigaku diffractometer with a Ni-filtered CuKα radiation. Particle morphology was observed by a JEOL transmission electron microscope (TEM). Thermal gravimetry (TG) and differential thermal analysis (DTA) curves were traced on a Rigaku thermoanalyzer at a heating rate of 10°C min⁻¹ under air stream. Nitrogen content was assayed by a Yanagimoto CHN elemental analyzer. Ca and P contents were determined with 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 N₂ adsorption isotherms measured by a Quantumchrome volumetric apparatus at the boiling temperature of liquid nitrogen fitting the BET equation. 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 N₂ adsorption and IR measurements, the samples were treated under 10⁻⁴ Torr at 300°C for 2 h.
RESULTS AND DISCUSSION

XRD patterns of the modified Hap showed only the peaks due to Hap and the crystallinity was essentially not influenced by this treatment. From the TEM observation, the unmodified Hap particles were rod-shaped and their average sizes were 70 nm (length) and 13 nm (width). The particle morphology evaluated from the TEM images was not altered by the modification and no new particles were generated. Further, the mean particle sizes of the modified samples nearly equal to those of original one. The molar ratio Ca/P of the materials were essentially not changed during the modification. The adsorption isotherms of N₂ on all the particles belonged to type II in the IUPAC classification. No remarkable change in the isotherms with raising the APS concentration was observed for the unmodified and modified particles. The specific surface area evaluated fitting the BET equation to the isotherms was almost not changed by the modification. These facts allow us to infer that the modification takes place only on particle surface.

In order to ascertain the degree of modification, the number of surface aminopropyl (NH₂(CH₂)₃-) group per unit surface area (nₐ), evaluated from the nitrogen content and specific surface area as a function of APS concentration was plotted in Figure 1. The nₐ steeply rises to 3.9 molecules nm⁻² with increasing the APS concentration up to 0.10 mol dm⁻³ and then slightly increases to 4.2 molecules nm⁻².

Thermal stability of the modified Hap was examined by thermal analysis. Figure 2 compares the TG and DTA curves traced under an air stream on the samples modified at various APS concentrations by solid and dotted lines, respectively. TG curve a of the unmodified material shows a continuous weight loss from room temperature to ca. 950°C, that is caused by the release of adsorbed and/or involved H₂O and H₂O formed in nonstoichiometric Hap via the reactions:¹⁶,¹⁷

\[ 2\text{HPO}_4^{2-} \rightarrow \text{P}_2\text{O}_7^{4-} + \text{H}_2\text{O} \ (200 - 500°C) \]
\[ \text{P}_2\text{O}_7^{4-} + 2\text{OH}^- \rightarrow 2\text{PO}_4^{3-} + \text{H}_2\text{O} \ (700 - 800°C) \]

Curves b - f of the modified materials show a weight loss between 220 and 500°C accompanying a DTA exothermic peak. The weight loss and exothermic peak increase by raising the APS concentration. Therefore, this weight loss can be ascribed to the
combustion of aminopropyl groups of the modified Hap. Whereas, the additional weight loss from 800 to 950°C appears in the curves c - f and it increases with increasing the APS concentration. This cause will be discussed later. To elucidate the surface structure of the modified Hap, we took IR spectra. Figure 3 displays the IR spectra traced in vacuo on Hap before and after modification with different concentrations of APS. Spectrum a of the original sample possesses a strong absorption band at 3570 cm\(^{-1}\) and a weak one at 3658 cm\(^{-1}\). The former band is due to the OH ions in the Hap lattice. The latter one has been assigned to the stretching vibration mode of surface P-OH groups generated from the protonation of surface PO\(_4^{3-}\) ions to maintain the surface charge balance of the Hap particle. Spectrum b of the sample modified with 0.01 mol dm\(^{-3}\) shows a weak surface P-OH band at 3658 cm\(^{-1}\), NH bands at 3338, 3275 and 3173 cm\(^{-1}\), and CH bands at 2930 and 2880 cm\(^{-1}\), while the lattice OH\(^-\) band is not changed by this modification. On increasing the APS concentration, the surface P-OH bands gradually weaken and the NH and CH bands developed (spectra c - e). To get further insight into the change of area intensity of surface P-OH, NH and CH bands by the modification, Figure 4 plots the area intensity of these bands against \(n_a\). The area intensity of surface P-OH band suddenly decreases at \(n_a \leq 2.4\) molecules nm\(^{-2}\) and is almost constant at \(n_a \geq 2.4\). Interestingly, the intensity of NH and CH bands linearly increases over the whole range of \(n_a\). It has been reported that the number of surface

FIGURE 2 TG-DTA curves of modified Hap. The solid and dotted lines represent TG and DTA, respectively. APS concentration (mol dm\(^{-3}\)): (a) 0, (b) 0.01, (c) 0.03, (d) 0.06, (e) 0.50, (f) 0.10.

FIGURE 3 IR spectra in vacuo of Hap modified with different APS concentrations. APS concentration (mol dm\(^{-3}\)): (a) 0, (b) 0.01, (c) 0.03, (d) 0.06, (e) 0.50, (f) 0.10.

FIGURE 4 Area intensity of surface P-OH, NH and CH bands against \(n_a\). The area intensity of surface P-OH band suddenly decreases at \(n_a \leq 2.4\) molecules nm\(^{-2}\) and is almost constant at \(n_a \geq 2.4\). Interestingly, the intensity of NH and CH bands linearly increases over the whole range of \(n_a\). It has been reported that the number of surface
P-OH groups of Hap assayed by the Grignard agent method was 2.6 groups nm\(^{-2}\). Assuming that the APS molecules react with only surface P-OH groups of Hap, maximum \(n_a\) value is 2.6 groups nm\(^{-2}\). Although, the \(n_a\) shown in Figure 1 exceeds the number of surface P-OH groups. These facts allow us to infer that the APS react with not only surface P-OH groups of Hap but also another sites.

From the above-described results, we can propose a mechanism involved in surface modification and thermal decomposition in air by Scheme 1. The ethoxy groups (\(-\text{OC}_2\text{H}_5\)) of APS hydrolyze to form Si-OH groups by reaction (1). The surface P-OH groups of Hap react with generated Si-OH groups to yield P-O-Si(OH)\(_2\)(CH\(_2\))\(_3\)NH\(_2\) groups and H\(_2\)O by reaction (2). Also, the formed surface -Si-OH groups react with Si-OH groups of APS by reaction (3), which is the same reaction compared to reaction (2). As a result, the \(n_a\) shown in Figure 1 was larger than number of surface P-OH groups. When the modified Hap was treated at 200 – 500°C, the surface -Si(OH)\(_2\)(CH\(_2\))\(_3\)NH\(_2\) group is combusted to form surface Si-(OH)\(_3\) group, CO\(_2\), NH\(_3\) and H\(_2\)O by reaction (4). On heating above 800°C, the surface Si-OH groups react with neighboring surface Si-OH groups to form surface Si-O-Si group and H\(_2\)O by reaction (5). Therefore, the increase of weight loss at 850 – 950°C shown in TG curves b - f of Figure 2 would be ascribed to the elimination of H\(_2\)O by reaction (5).

Summary of the results obtained in this study can be written as follows. The surface of Hap could be modified with APS without changing its structure, crystallinity,
molar ratio Ca/P and particle morphology. The $n_a$ increased from 0 to 4.2 molecules nm$^{-2}$ with increasing the APS concentration. The APS reacted with surface P-OH groups of Hap and formed -Si-OH groups by the reactions (1) – (3) in Scheme 1.

REFERENCES