Preparation of Monetite ($CaHPO_4$) with Hexagonally Packed Mesoporous Structure by a Sol–Gel Method Using Cationic Surfactant Aggregates as a Template

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We first-successfully fabricated mesoporous calcium phosphates by a regular sol–gel method using cationic surfactant aggregates as a template. Low-angle XRD and TEM observation indicated that a product included hexagonally packed mesoporous structure. Wide-angle XRD and FT-IR observation identified the product as monetite ($CaHPO_4$), which is one of calcium phosphates.

Mesoporous silica systems with uniformly sized pores, e.g., MCM-41 and MCM-48, have been successfully synthesized by a liquid crystal templating mechanism.[1–5] In this mechanism, cooperative self-assembly of inorganic substances and cationic surfactants first forms a liquid crystal phase to establish an ordered array; subsequent thermal processes remove the surfactant molecules, leaving well-organized inorganic mesoporous structures. Mesoporous materials with nanometer-sized pores are characterized by larger specific surface and pore volume and have been applied in wide range of fields: catalysis, polymerization, adsorption, separation, photochemistry, etc.

Calcium phosphates, such as tricalcium phosphate, hydroxyapatite, etc., are known to be bioactive bioceramics, which can chemically combine with hard tissues in the human body.[6–9] However, mesoporous materials composed of calcium phosphates have been received little attention. Recently, mesoporous materials are observed to adsorb bioactive substances, for example, proteins and anticancer drugs, into their pores, expected as carriers for controlled delivery of drugs.[10] Therefore, mesoporous calcium phosphates combining both bioactivity and drug delivery would be useful to provide three-dimensional scaffolds for tissue engineering and bioceramic implants including growth factors to give osteoinductive property.

In the present study, we report the first approach to fabricate hexagonally packed mesoporous calcium phosphates by a regular sol–gel method using cationic surfactant aggregates as a template. We determined their characteristics by means of X-ray powder diffractometry (XRD; RINT 2500VHF, RIGAKU) with Cu Kα radiation and by Fourier transform infrared spectroscopy (FT-IR; FT/IR-460 Plus, JASCO) with the KBr method. The morphology of the mesoporous calcium phosphates was observed by transmission electron microscopy (TEM; JEM-1011, JEOL) and scanning electron microscopy (SEM; JSM-5500LV, JEOL).

We prepared mesoporous calcium phosphates, with referring to the sol–gel method originally reported by Liu et al.[11] A 3.99 g of triethyl phosphite ($(C_2H_5O)_3P$) was first dissolved in 10 mL of distilled water by stirring vigorously for an hour. A given amount of cetyltrimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3Br$, CTAB) and 6 mL of distilled water containing 9.45 g of calcium nitrate ($Ca(NO_3)_2$) were added into the solution, followed by standing for 24 h at a room temperature. The solution was dried at 90 °C for 48 h to get white precipitate, and the precipitate was filtered off and washed with distilled water and ethanol to remove the surfactant molecules. Finally, the precipitate was dried at 110 °C for 24 h to get mesoporous calcium phosphates.

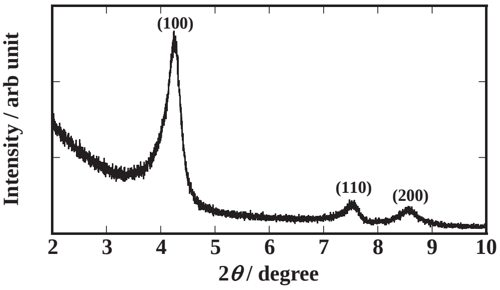

Figure 1. Low-angle XRD pattern of precipitate prepared with 2.63 g of CTAB.

We measured low-angle XRD of the precipitate prepared with various content of CTAB. At a lower CTAB content, no peak was observed, whereas a few peaks at 2θ of 4.24, 7.57, and 8.58° were determined at a CTAB content more than 2.18 g. For example, Figure 1 shows the XRD pattern of the precipitate fabricated with 2.63 g of CTAB. The *d* spacing values calculated from the peaks are 2.08, 1.17, and 1.03, and the *d* spacing ratio of each peak to the first maximum peak in the precipitate system is similar to that in hexagonally packed mesoporous silica system, MCM-41, which is produced by using CTAB aggregates as a template.[12] This finding indicates that the precipitate possesses a hexagonally packed mesoporous structure, as well as MCM-41.

In addition, TEM and SEM micrographs of the precipitate fabricated by 2.63 g of CTAB are exhibited in Figures 2a, 2b, and 2c. We can find almost hexagonal symmetry of pore arrangement (Figure 2a) and numerous lines aligning (Figure 2b) that are probably frameworks between two cylindrical channels of the hexagonal structure. This structure seems to be unstable under electron-beam-irradiation condition and was distorted during high-magnification TEM observation by electron-beam-irradiation. In order to avoid the distortion, we carefully carried out TEM observation as soon as possible. Compared with pore diameter estimated from the low-angle XRD measurement, the pore diameter in Figure 2a is quite larger. The enlargement of pore diameter may be due to the distortion of the pore structure with electron beam irradiation. Moreover, Figure 2c shows SEM micrograph of the precipitate. We can see stacked layer structure in the precipitation.

From the low-angle XRD and TEM observation, therefore, we consider that the precipitate produced by the regular sol–gel method using $(C_2H_5O)_3P$ and $Ca(NO_3)_2$ with CTAB includes hexagonally packed mesoporous structure.

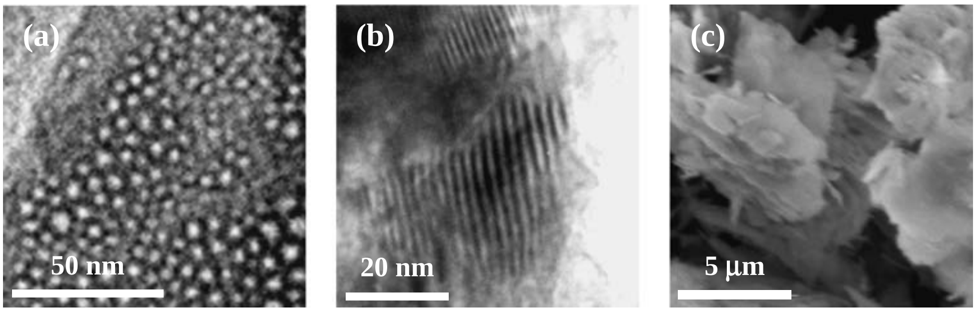

Figure 2. TEM (a and b) and SEM (c) micrographs of precipitate produced by 2.63 g of CTAB.

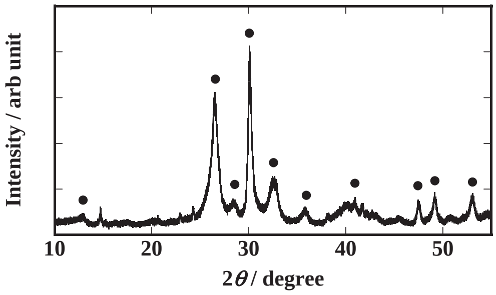

Figure 3. Wide-angle XRD pattern of precipitate prepared with 2.63 g of CTAB. The marked peaks are assigned to monetite.

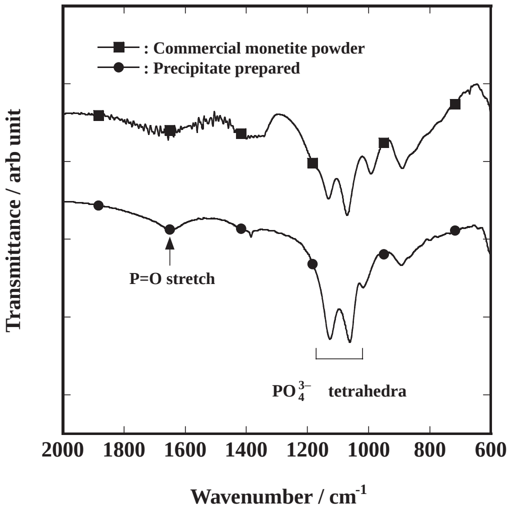

Figure 4. FT-IR spectra of precipitate prepared with 2.63 g of CTAB and commercial monetite powder.

Figure 3 depicts a wide-angle XRD pattern of the precipitate prepared with 2.63 g CTAB. Compared with the standard database and literature reference,[13,14] the XRD pattern are characteristic of monetite ($CaHPO_4$), which is one of calcium phosphates. In addition, Figure 4 represents a FT-IR spectrum in fingerprint region of the precipitate. An FT-IR spectrum of commercial monetite powder, which was purchased from Aldrich Co., is also shown in this figure. The spectrum of precipitate is similar to that of commercial monetite. The peaks from 1000 to 1200 cm^{-1} is characteristic of PO_4^{3-} tetrahedral; the peak around 1650 cm^{-1} is assigned to P=O.[14] The wide-angle XRD and FT-IR observation then indicate that the precipitate is identified as monetite. And furthermore, the frameworks between cylindrical channels of the hexagonal structure are considered to be monetite by consideration of the fact that there is no main peak except for the peaks of monetite in the wide-range XRD and the FT-IR measurements.

As a result from a series of our observations, in conclusion, we first-successfully demonstrate the fabrication of monetite, which is a kind of calcium phosphates, with a hexagonally packed mesoporous structure by a regular sol–gel method using cationic surfactant aggregates as a template. In general, monetite has been used as calcium phosphate cement for a substitute material in orthopedic surgery,[15] but it cannot chemically combine with hard tissues in itself. So that, further studies are in progress to fabricate a kind of calcium phosphates with bioactivity, especially tricalcium phosphate and hydroxyapatite, by a sol–gel method using surfactant aggregates, with referring to this study.

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