



# Mesoporous silica formation on hydroxyapatite nanoparticles



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## ABSTRACT

The additive effect of TEOS and CTAB on the HAp crystal growth and HAp/silica hybrid shape was investigated. The mesoporous silica formation on the HAp nanoparticles was successfully achieved, and the  $S_{\text{BET}}$  and  $R_{\text{BJH}}$  values were changed with the feed Ca/P ratio. The HAp/silica hybrids exhibited the higher  $S_{\text{BET}}$  values with the mesopores. It was suggested that the silica phase specifically interacted with the  $a$ -plane of HAp and subsequently the HAp along with the  $c$ -axis direction to be anisotropic hybrid shapes.

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## 1. Introduction

Calcium phosphate (CP) compounds are the main components of teeth and bones and exhibit biocompatibility [1–4]. In particular, hydroxyapatite (HAp) has widely been studied for artificial bones and dental implants [4–6], and is expected to be used for a wide range of the biomedical applications [7,8]. The regularly-arranged nanostructures have been found to also have the biocompatibility [9,10]. Thus, the formation of mesopores with the diameter of 2–50 nm has attracted attention. Therefore, it is important to design the nanostructures for the applications such as drug delivery system (DDS) and cell culture substrates [10].

In order to prepare the CP nanostructures, a supramolecular templating method using surfactants has widely been investigated [11–15]. In the synthesis by a cationic surfactant, the pore diameter was 5.5 nm and the lower specific surface area was 11.3 m<sup>2</sup>/g [11]. In the synthesis by an anionic surfactant, the periodic lamellar structures with alternating CP-by-surfactant layers has been laminated [12], and the brushite with a wormhole-like structure has also been synthesized [13]. In the synthesis by a nonionic surfactant, the porous CP with the pore size of 13.5 ± 3.5 nm and the higher specific surface area of 263 m<sup>2</sup>/g was prepared [14], and the CP with the larger pore size of 48–73 nm and the specific surface area of 57–73 m<sup>2</sup>/g has also been synthesized [15]. Regardless

of the researches, the innovative and designed CP nanostructures have not been completed for the significant applications.

The amorphous silica based on the sol-gel reactions among silicon alkoxide molecules is easy to form the periodic nanostructures [16], and exhibits the low biological toxicity [17,18]. In particular, mesoporous silicas with biocompatibility [9,10] have been prepared as follows; the siliceous phase in the solution can rapidly precipitate on the cationic surfactant micelles and subsequently mesoporous structures can be formed by the calcination [19,20]. Thus, the preparation CP nanostructures through the mediation of the amorphous silica precipitation on the surfactant micelles would make it possible to achieve the novel biocompatible materials. Based on the viewpoints, the biomimetic construction of CP-silica components has been reported for the biomedical applications [25,29]. Although the investigation of the hybrid functions and interfaces is important for providing two-step dissolution in biological solution. there has been no investigation on the controllable interfaces between CP-silica.

In this study, the nanostructured hybrids of the CP with silica phases were prepared through the mediation by the reactivity of silicon alkoxide as show in Fig. 1 (Illustration). Then, the nanostructures of the particles were evaluated depending on the ratio of calcium to phosphorus (Ca/P) during the synthetic process.

## 2. Materials and methods

The CP nanostructured hybrids were synthesized as follows. 5.02 mmol of cetyltrimethylammoniumbromide (CTAB) was

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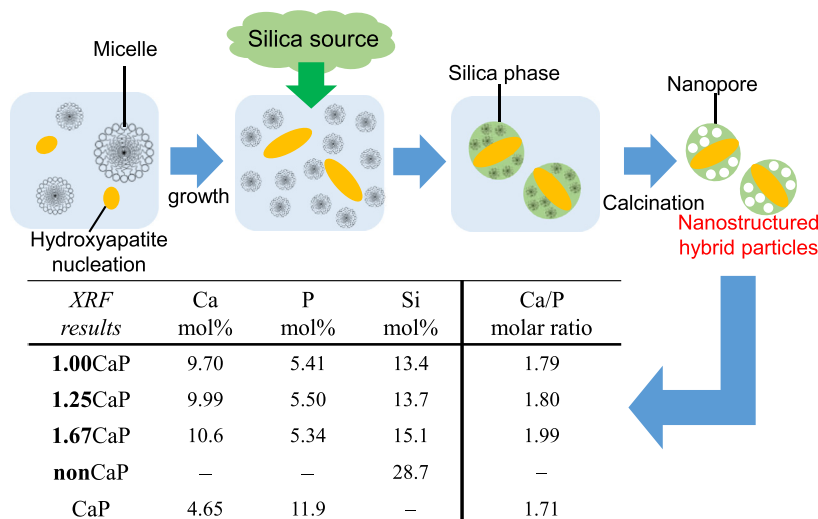


Fig. 1. Illustration of the synthetic outline of this study, and the elemental concentrations and Ca/P molar ratios obtained from the XRF measurement.

completely dispersed into 23.6 mL of ultrapure water (1.31 mmol).  $K_2HPO_4$  at the different amounts of 12.0, 9.6 and 7.2 mmol was dissolved into the CTAB solution to form the micelle, in which the formation and reaction mechanism has been reported by our group [27], and the solution pH was adjusted to 12 by 25 wt% of tetramethylammonium hydroxide (TMAOH). 23.6 mL of the aqueous solution containing  $CaCl_2 \cdot 2H_2O$  (12.0 mmol) was added into the CTAB/ $K_2HPO_4$  solution at the drop rate of 1.0 ml/min. The solution in poly(propylene) vessel was continuously stirred at 40 °C for 24 h. Then, 128.0 mmol of NaOH and subsequent 19.2 mmol of tetraethoxysilane (TEOS) were added into the solution, and the solution was sealed in a Teflon-lined autoclave and hydrothermally mixed at 100 °C. The white-colored precipitation was centrifuged, washed by ultrapure water, and dried at 65 °C for 12 h, calcined at 250 °C for 3 h and subsequent 550 °C for 6 h. The resulting powders prepared by the added  $K_2HPO_4$  amounts of 12.0, 9.6 and 7.2 mmol were defined as 1.00CaP, 1.25CaP and 1.67CaP, respectively. As the references, the samples prepared under the same synthetic procedure without calcium phosphate and without TEOS by the added  $K_2HPO_4$  amounts of 12.0 mmol were defined as nonCaP and CaP, respectively.

The characterization was conducted using wavelength dispersive X-ray fluorescence (XRF) spectrometry,  $\theta$ - $2\theta$  scanning out-of-plane X-ray diffraction (XRD) meter, nitrogen ( $N_2$ ) adsorption and desorption equipment, Brunauer-Emmett-Teller (BET) [21] surface areas and Barrett-Joyner-Halenda (BJH) [22] pore sizes were calculated. Field emission scanning electron microscope (FE-SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron micrographs (TEM), and zeta potential measurement. In the XRD, the crystallite size ( $D_{hkl}$ ) was calculated from Scherrer's equation ( $K = 0.9$ ) using the diffraction  $2\theta$  and half width of 300 and 002 patterns.

The streaming potential ( $U_{str}$ ) and zeta potential ( $\zeta$ ) were measured as described in Table S2 (ESI) and calculated from the following Eq. (1) [24].

$$U_{str}/\Delta p = (\epsilon_{rs}\epsilon_0\zeta)/(\eta\lambda) \quad (1)$$

where  $\Delta p$  is the pressure difference between the two terminal parts in capillary,  $\epsilon_0$  is the electric permittivity under vacuum,  $\epsilon_{rs}$  is the relative permittivity of the solvent,  $\eta$  is the dynamic viscosity of the liquid, and  $\lambda$  is the relative permittivity of the solution.

### 3. Results and discussion

Fig. 1 shows the resultant chemical compositions of the hybrids and references, which were measured by an XRF. The hybrids significantly contained the Ca, P and Si elements. The resultant Ca/P molar ratio (1.79–1.99) of the hybrid was higher than that of the feed Ca/P molar ratio. As shown in Table S1 (ESI), the various elements used in the synthesis were detected. Taking into account that the negatively-charged TEOS inhibited the phosphate ion incorporation behavior in the hybrid process, it is indicated that the various elements would be included in the hybrids to decrease the incorporated P amount (i.e., the increase in the resultant Ca/P ratio). Moreover, the preparation under the existence of CTAB molecules would change the charge compensation states in/on the HAp crystal structures to include the  $CO_3^{2-}$  ions. In fact, the carbonate ion ( $CO_3^{2-}$ ) bands were recognized by a Fourier transform infrared spectroscopy at  $870\text{ cm}^{-1}$  and  $1400\text{--}1500\text{ cm}^{-1}$ , which would come from the atmospheric carbon dioxide. In the EDS elemental mapping images of the hybrids (ESI, Fig. S1), the existence of Si, P, Ca and O elements exhibited along with the particle shapes in FE-SEM images, and the each element was in the same place at the micrometer scales, although the Ca and P were not from non-CaP and Si element was also not from CaP. Therefore, the silica was hybridized with the Ca-rich CP.

Fig. 2 shows the XRD patterns of the hybrids and references. The patterns of the hybrids and CaP were attributed to a single phase of HAp ( $Ca_5(PO_4)_3(OH)$ , ICDD:00-009-0432). Since the amorphous halo pattern was also observed from the hybrids and nonCaP, indicating the hybridization between HAp and silica. From the pattern shapes, the HAp in the hybrids has low crystallinity. The crystalline sizes of  $D_{002}$  and  $D_{300}$  were 30.1 and 7.3 nm for 1.00CaP, 30.6 and 9.2 nm for 1.25CaP, 31.6 and 6.8 nm for 1.67CaP, which were clearly different from the sizes (27.8 and 22.5 nm) for CaP, indicating the significant inhabitation of HAp crystal growth along with  $a$ -axis. It was suggested that the negatively-charged TEOS specifically interacted with the  $a$ -plane of HAp crystals. The nonCaP alone indicated the diffractions indexed as 100, 110 and 200 reflections of a hexagonal structure and the  $d$ -spacing values are 3.3, 1.9 and 1.6 nm, respectively. Therefore, the additive effect of TEOS on the HAp crystal growth was significantly observed.

Fig. 3 shows the nitrogen adsorption and desorption isotherms and BJH pore size distributions. According to the IUPAC classification [23], the isotherm and hysteresis classifications in 1.00CaP

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