



Controlling the pore characteristics of mesoporous apatite materials: Hydroxyapatite and carbonate apatite

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Abstract

Mesoporous hydroxyapatite (HA) and carbonated hydroxyapatite (CHA) were synthesised through the soft template route by using ionic surfactants, namely decyltrimethylammonium bromide (C10TAB) and hexadecyltrimethylammonium bromide (C16TAB), and non-ionic surfactants, namely P123 and F127. After calcination at 550 °C, a porous structure, with pore sizes varying from 2 nm to 49.2 nm and with a specific surface area ranging from 21 to 73 m²g⁻¹, was formed with different surfactants. The axial view of the TEM images revealed that the pores formed within the particles were distributed randomly. The continuous pH-control technique and high water ratio may produce mesopores with better pore characteristics. Meanwhile, surfactants with a longer hydrophobic alkyl are expected to produce HA with larger pores but with a lower surface area. A higher surface area was observed for CHA synthesised with triblock co-polymers surfactants of a higher propylene oxide (PO) unit.

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1. Introduction

Ever since the discovery of the Mobil Composition of Matter no. 41 (MCM-41) in 1992 [1], porous materials have become a major topic for research. In 1994, the International Union of Physical and Applied Chemistry (IUPAC) released the standard definition of pore size, where micropores are smaller than 2 nm in diameter, mesopores are 2–50 nm and macropores are larger than 50 nm [2]. With the emergence of nanotechnology, micro-, meso- and macropores can also be described as nanoporous materials as their pore sizes are found between 1 and 100 nm, which fall within the nanoscale range.

Porous hydroxyapatite (HA) is the promising candidate to serve as a drug carrier. The initial study on porous HA began with macroporous HA (pore width > 50 nm) [3,4]. Macroporous HA is suitable for use as drug delivery system because: (a) it is biocompatible, (b) different pore sizes can be introduced within the nanoparticles, in order to control the release rate of the drug [5] and (c) it does not change the chemical structure of the drug [3]. However, a study by Radin and his co-workers has demonstrated that the ‘burst’ release profile exhibited by macroporous HA is a major drawback for its use in controlled release drug applications [5]. Palazzo et al. confirmed that the low porosity of HA showed an even more initial burst release, which is a sudden release of a drug in large amounts at the initial stage of the delivery period. This behaviour is caused by the tendency of the drug molecules to concentrate on the external macropore walls rather than on the internal pores [6]. A smaller surface area and lower porosity increases the possibility of such a phenomenon

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occurring, because it is difficult for the drug molecules to reach the internal pores and to be adsorbed by the limited surface area. Thus, the mesoporous HA, which has a higher porosity and smaller pore size, is needed in order to increase the surface area and to allow more drug molecules to enter the pores.

However, the major inorganic composite of natural bones and teeth is carbonated hydroxyapatite, the impure and nonstoichiometric version of HA [7]. Carbonated hydroxyapatite (CHA) is nonstoichiometric, with a chemical formula, $\text{Ca}_{10-x/2}[(\text{PO}_4)_6-x\text{CO}_3]_x[(\text{OH})_{2-2y}(\text{CO}_3)_y]$, where x and y are numbers of CO_3^{2-} ions substituting for PO_4^{3-} and OH, respectively [8]. The substitution of carbonate is known to weaken the apatite structure and make it more soluble [9]. Therefore, the synthetic carbonated hydroxyapatite (CHA), which is chemically more similar to human bone constituents, has therefore shown to improve biocompatibility, bioactivity, and resorbability [7,10], compared to HA. For this reason, a better profile of drug adsorption and release is expected from CHA.

Because pore size is the crucial factor that determines the performance of the mesoporous hydroxyapatite as an adsorbent and drug carrier material, various synthesis methods have been utilised to produce mesoporous HA. So far, based on published works, mesoporous HA can be synthesised by the sol-gel [11] and co-precipitation methods (i.e., by soft-templating [12–15] and hard-templating) [16]. Soft-templating involves the utilisation of a surfactant as a structure directing agent. The advantages of the soft-template method are: (a) it is able to create pores within the mesopore range; (b) the pore size can be controlled by varying the synthesis temperature and carbon chain length of the cationic surfactant; (c) it is a simple synthesis procedure; (d) the chemicals are easily available; (e) simple apparatus is required for the experiment. Therefore, the soft-template method is still the most promising method for use in the synthesis of mesoporous hydroxyapatite (HA) and carbonated hydroxyapatite (CHA).

Initially, surfactants that have commonly been used in the synthesis of HA are ionic type [13,14]. However, ionic surfactants such as cationic alkyltrimethylammonium, anionic alkylsulfonates or alkylphosphates have some drawbacks as pore templates, for example: (a) the wall thickness of the pores produced is between 0.8 and 1.3 nm and this limits the stability; and (b) the pore size created by the surfactant is very limited [15,17]. These two main limitations have caused researchers to resort to non-ionic surfactants [15,18] as another option for structure directing agents.

Thus, in this paper, we described the synthesis process of mesoporous HA and CHA either by using ionic or non-ionic surfactants. The main objectives of this present study is to investigate the effect of various synthesis parameters such as water ratio, pH control techniques, carbon chain length and PEO/PPO unit of the surfactants on the pore characteristic and sorption properties on mesoporous HA and CHA.

2. Control of pore characteristics of mesoporous hydroxyapatite

Several researchers used cetyltrimethylammonium bromide (with different carbon chain lengths) as the ionic surfactant

[13,14]. Ionic surfactants can be dissolved in an aqueous solution, namely water. The surfactants are controlled at high concentrations to form micelles, which may be spherical, elliptical, rod-like or vesicular. The micelles serve as templates for the precipitation of the HA (inorganic species). A calcium precursor of HA is added into the solution, followed by the addition of a phosphate precursor. A surfactant-HA complex is formed from a series of interactions between the precursors and the surfactant micelles, and this is known as a co-operative self-assembly. The interactions lead to the formation of a white precipitate with an ordered nanoscale structure. During the mixing process, the alkalinity of the solution is maintained at pH 11 or 12. The solution is then aged at a certain temperature and for a period of time. The precipitates are then derived from the solution and dried in an oven, before being calcined to combust the surfactant micelles, in order to reveal the pores.

2.1. pH-control techniques

The pore characteristics of mesoporous HA were found to vary when different pH-control techniques were employed in the synthesis process (Table 1). The cationic surfactant used to synthesise the mesoporous HA was decyltrimethylammonium bromide (C10TAB) (Tokyo Chemical Industry). Sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) from Merck were used as the phosphate and calcium precursors, respectively. The pH of the mixture was controlled using sodium hydroxide (NaOH). The synthesis process was discussed in detail in our previous published work [19]. In the continuous pH-control technique, the pH of the solution was maintained at 11 by dropping NaOH throughout the mixing of the surfactant-phosphate solution and the calcium solution, while in the initial pH-control technique, the pH of the surfactant-phosphate solution was set at 11 before mixing with the calcium solution. The continuous pH-control technique was able to produce a higher surface area and a more uniform pore size distribution (PSD) of mesoporous HA, but lower crystallinity compared to the initial pH-control technique. The crystallinity in this study was calculated using the following equation [20, 21].

$$X_c = 1 - \frac{V_{112/300}}{I_{300}} \quad (1)$$

where X_c is the fraction of crystalline phase; I_{300} is the intensity of (300) reflection; $V_{112/300}$ is the intensity of hollow between (112)

Table 1
Parameters involved in a study of the effect of the pH control technique on pore characteristics [19].

Sample	Surfactant	Ageing duration (h)	pH-control technique	Water ratio for CTAB – phosphate: calcium solution	Crystallinity
P	No	24	Initial	3:5	0.9169
P1	C10TAB	24	Initial	3:5	0.8164
P2	C10TAB	24	Continuous	3:5	0.6839

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