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Fabrication and characterization of 1D brushite nanomaterials via sucrose ester reverse microemulsion

HongNgee Lim [a,*], Anuar Kassim [a], NayMing Huang [b], Rauzah Hashim [c], Shahidan Radiman [d], PoiSim Khiew [e], WeeSiong Chiu [e]

[a] *Chemistry Department, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia*
[b] *Physics Department, Faculty of Science, Universiti Malaya, 50603 Kuala Lumpur, Malaysia*
[c] *Chemistry Department, Faculty of Science, Universiti Malaya, 50603 Kuala Lumpur, Malaysia*
[d] *School of Applied Physics, Faculty of Science and Technology, University Kebangsaan Malaysia, 43000 Bandar Baru Bangi, Selangor Darul Ehsan, Malaysia*
[e] *Faculty of Engineering & Computer Science, Nottingham University, Jalan Broga, 43500 Semenyih, Selangor Darul Ehsan, Malaysia*

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Abstract

In the present study, 1-dimensional (1D) brushite nanomaterials were fabricated through sucrose ester based reverse microemulsion for the first time. X-ray diffraction patterns revealed that the nanomaterials possessed brushite crystal phase with trace amount of hydroxyapatite. The size and morphology of brushite crystals were governed by the changes in the aqueous-to-sucrose ester weight ratio at low initial reactant concentration, giving rise to rod-like and fibre-like 1D nanomaterials. Brushite nanorods and nanofibres with average diameters of 25.53 ± 4.60 nm (aspect ratio ~ 6) and 76.18 ± 19.74 nm (aspect ratio ~ 40), respectively, had been synthesized. As the reactant concentration increased, it became the key factor in controlling nucleation and crystal growth, rendering the aqueous-to-sucrose ester ratio unimportant. Formation mechanism of various morphologies of brushite crystals is postulated.

Keywords: Calcium phosphates; Brushite; Sucrose ester; Microemulsion; Low dimensional nanomaterials

1. Introduction

Bone is a highly metabolically active tissue; remodelling continues throughout life. The remodelling process is an active coupling of the processes of bone formation and resorption [1] sustained by the regulated action of osteoclasts and osteoblasts [2]. Calcium phosphates constitute the major inorganic phase of bone, are bioactive and can be rapidly integrated into the human body [3,4]. Therefore, they are of high relevance to material science, biology and medicine.

Calcium orthophosphates are salts of tribasic phosphoric acid, H_3PO_4 and its ionic compounds. Hydroxyapatite $Ca_5(PO_4)_3(OH)$, octacalcium phosphate $Ca_8H_2(PO_4)_6{\cdot}5H_2O$, monetite $CaHPO_4{\cdot}2H_2O$, and brushite $CaHPO_4{\cdot}2H_2O$ are different crystalline orthophosphates that have been extensively studied for their relevance in biological mineralization [5]. Brushite has raised considerable interest amongst researchers in bone substitution due to their fast resorption as it is a metastable compound when used under physiological conditions [6–8]. The biocompatibility and degradation of brushite have been demonstrated in several in vitro and in vivo studies [9–11]. Following immersion in aqueous media, brushite may, depending on conditions, be stable, disintegrate or dissolve and precipitate as hydroxyapatite [12].

As the natural bone is made of calcium phosphate nanoparticles scattered in the organic matrix [13], it is believed that deliberate tailoring of the crystallite size, morphology, stoichiometry and composition of calcium phosphates could lead to improved properties such as bioactivity, biocompatibility, surface area, chemical and physical stability and mechanical properties by adjusting the concentration of reactants, concentration of surfactants, pH and temperature [14–16]. The different forms of particulate calcium phosphates manufactured and sold in the market include irregular

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* Corresponding author. Tel.: +60 163301609; fax: +60 358911088.
E-mail address: janet_limhn@yahoo.com (H. Lim).

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multifaceted particles and smooth rounded particles, with solid or porous structure [17]. They are osteoconductive and help in growth and attachment of bone [18,19], and are clinically used in oral surgical procedures to augment the alveolar ridge [20] and in periodontal repair [21]. Kent et al. [22] reported improved denture stability and retention when dense calcium phosphate particles have been used for augmentation of atrophic mandibular and maxillary alveolar ridges.

Many researchers have explored fabrication of calcium phosphate nanoparticles of various morphologies such as lath [16], rod [23], belt [24], sheet, needle [25], wire [26], and cone [27]. Among the processing routes used to fabricate the nanoparticles are sol–gel [14], solid state [28], biosynthesis [29], chemical precipitation [5], hydrothermal [30,31], hard templating [23], emulsion [32,33] and microemulsion [16].

Reverse microemulsion is a well-known processing route in the fabrication of calcium phosphate nanoparticles. Surfactant stabilized discontinuous aqueous phase acts like a nanoreactor that can control nucleation and crystal growth in restricted geometries [34–36]. Surfactants that have been used to stabilize microemulsion for preparation of calcium phosphate nanoparticles are tricaprylmethylammonium chloride [16], sorbitan monooleate [25], polyoxyethylene sorbitan monooleate [37] and octaethylene glycol monododecyl ether [38].

In this paper, we utilized sucrose ester S1670 as nonionic food grade biosurfactant to form water-in-oil (w/o) reverse microemulsion (water/heptan-1-ol/sucrose ester) as a soft template for the synthesis of brushite crystals. To the best knowledge of the authors, no work has been reported using sucrose ester as biosurfactant in reverse microemulsion for the synthesis of brushite nanoparticles. These surfactants are biodegradable and formed from renewable resources such as fatty acids and sugars. In order to monitor changes in nucleation and crystal growth, reactant concentration and water-to-surfactant weight ratio (*W*/*S*) were considered. Based on the experimental results, plausible formation mechanism of the brushite crystals is discussed.

2. Experimental

2.1. Materials

The starting materials used in this work were calcium chloride dihydrate, $CaCl_2{\cdot}2H_2O$ (Sigma–Aldrich), disodium hydrogen phosphate, Na_2HPO_4 (Sigma–Aldrich), heptan-1-ol (Merck) and food grade sucrose ester (Mitsubishi-Kagaku Foods Corporation). The sucrose ester used in this work is a commercially available sucrose monoester of stearic acid (S1670, HLB = 16, at least 70% monoester of stearic acid) in a mixture of di-, tri- and polyesters of stearic acids. All reagents were of analytical grade and were used as received. Deionized water ($\geq$18.2 MΩ) was used throughout the study.

2.2. Fabrication of calcium phosphate crystals

Sucrose ester was mixed thoroughly with heptan-1-ol (sucrose ester-to-heptan-1-ol weight ratio equivalent to 0.80) using a vortex mixer. $CaCl_2{\cdot}2H_2O$ aqueous solution was added into the above mixture followed by Na_2HPO_4 aqueous solution under constant stirring with predetermined amount of aqueous-to-surfactant weight ratio (*W*/*S*) to form a transparent reverse microemulsion. The calcium-to-phosphate molar ratio is 1.67, similar to that of natural bone and teeth [39]. The microemulsions were aged at 40 °C for seven days. After aging, the microemulsions were demulsified with ethanol (98%, Fluka). The white precipitates were washed with ethanol and deionized water until they were free from organic matter. All the precipitates were calcined at 600°C for 2 h. The calcium phosphate crystals were prepared in reverse microemulsion containing *W*/*S* = 0.25, 0.40 and 0.60 with $CaCl_2{\cdot}2H_2O$:Na_2HPO_4 concentrations of (I) 0.10 M:0.06 M, (II) 0.30 M:0.18 M and (III) 0.50 M:0.30 M, respectively. Bulk calcium phosphate was prepared using conventional wet chemical processing route whereby 0.50 M $CaCl_2{\cdot}2H_2O$ aqueous solution was titrated with 0.30 M Na_2HPO_4 aqueous solution under constant stirring as a comparison to the reverse microemulsion-prepared calcium phosphates.

2.3. Characterization of calcium phosphate crystals

Crystallinity of the calcium phosphate powders was measured using a Phillips X-Ray Diffractometer (XRD). Measurements were taken from 15° to 70° on the 2θ scale at a size step of $0.033^\circ\ s^{-1}$. The Cu anode X-ray was operated at 40 kV and 30 mA in combination with a Ni filter to give monochromatic Cu Kα radiation at 1.54 Å. Qualitative analysis was performed with Xpert HighScore using the JCPDS PDF-2 database [40]. Chemical bonding of the powders was analyzed using a Perkin Elmer Fourier Transform Infrared (FTIR) spectroscopy. The powders were mixed with potassium bromate, ground homogenously and converted into pellets. The spectra (% transmittance with wavenumber) were recorded. Size and morphology of the powders were observed using a Phillips HMG 400 Transmission Electron Microscopy (TEM) under 100 kV accelerating voltage and a LEO 1455 Variable Pressure Scanning Electron Microscopy (SEM). Samples for TEM observation were dispersed in ethanol and sonicated for five minutes to avoid aggregations. The mixtures were then placed on carbon-coated 400 mesh copper grids and dried at room temperature overnight before examination. Samples for SEM observation were mounted on aluminum stubs using double-sided tape and vacuumed coated with gold in a Polaron SC500 sputter coater.

3. Results and discussion

Fig. 1 shows the XRD patterns of bulk (a) and reverse microemulsion-prepared calcium phosphates (b), which portrayed almost similar diffraction profiles. The diffraction peaks of the crystals are indexed to brushite crystal structure (JCPDS file no. 2-0085) with trace amount of hydroxyapatite. No characteristic peaks of other calcium phosphate phases and impurities are detected. The intensity of the diffraction peaks indicates that the samples were well crystallized. Low pH and