

Synthesis of calcium phosphate nanoparticles in deep-eutectic choline chloride–urea medium: Investigating the role of synthesis temperature on phase characteristics and physical properties

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Abstract

A novel and green method based on precipitation of calcium phosphate reactants in a deep eutectic solvent (DES) was devised for the synthesis of calcium phosphate nanoparticles. The DES was prepared by simple mixing–heating of choline chloride and urea. The effect of synthesis temperature on particulate and structural properties of the synthesized calcium phosphate nanoparticles was examined by X-ray diffractometry, field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy and nitrogen adsorption techniques. Based on the results, increase of synthesis temperature from 25 to 150 °C was associated with the gradual evolution of calcium-deficient apatite phase, however with a poor degree of crystallinity. The particle size and Ca/P molar ratio of precipitated calcium phosphate particles were also dependent of temperature so that they increased from 25 to 85 nm and 1.10 to 1.27 when the synthesis temperature increased from 25 to 150 °C. The synthesized particles were mesoporous regardless of the synthesis temperature. Given the advantages of DESs from both environmental and chemical points of view, the present study can provide a new direction for DES-assisted synthesis of inorganic nanomaterials and particularly nanobiomaterials.

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1. Introduction

Calcium phosphates (CaPs) are a class of bioceramics that is found throughout the body of vertebrates in the form of amorphous and crystalline phases [1,2]. Hence, synthetic CaP bioceramics are vastly employed for dentistry and orthopedic purposes owing to their superior biocompatibility, nontoxicity, bioactivity, and chemical/crystallographic resemblance to hard tissues [3–8]. In addition, it is well established that nanosized and nanocrystalline CaPs clearly represent improved bioactivity and biocompatibility leading to enormous applications of nano-CaPs in biomedical area [2]. Accordingly, numbers of researchers have focused on the synthesis of nano-CaP topic. To date, various synthesis methods have been developed for nano-CaPs including

sol–gel, solution spray drying, hydrothermal process, precipitation techniques, solid-state reaction, and biomimetic deposition [9–15].

Synthesis of amorphous calcium phosphates (ACPs), one of the most frequent forms of CaPs has been much considered because, compared to other forms of calcium phosphates, ACPs exhibit adequate in-vivo biodegradability and bioactivity. ACPs show an identical glass-like structure in which there is no long-range order of the atomic planes meanwhile they exhibit variable chemical properties. The Ca/P molar ratio of ACPs is less than 1.5 which is lower than that of apatite (1.67) [16,17]. Like other CaPs, ACPs are also synthesized by two main approaches: low-temperature wet chemical method using water or water–alcohol medium (e.g. precipitation [18] and sol–gel [19]) and dry route using high energy processes and high temperatures (e.g. flame spray pyrolysis [20], mechano-chemical method [21] and rapid quenching of melted calcium phosphates [22]). Generally, the use of solvents with high

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vapor pressure, surfactants, stabilizers, high calcination temperature and expensive precursors makes these methods uneconomical and harmful. Thus, development of simple, cost-effective and eco-friendly synthesis method is an important issue.

Deep eutectic solvents (DESs) are an emerging class of benign solvents that regarded as green ionic liquid (IL) analogs with similar physicochemical properties such as high conductivity, polarity, thermal stability, and negligible vapor pressure [23,24]. However, DESs possess some additional advantages over ILs, e.g. low cost, biocompatibility and simple preparation method without the need for purification [25]. DESs can be simply prepared by mixing a quaternary ammonium salts (e.g. choline chloride, ChCl, which is being used as vitamin B4 in chicken food) with a metal salt, hydrated salts or hydrogen bond donors (HBD) such as amines, amides, polyalcohols, organic acids and carbohydrates [26,27]. In fact, reduction of the electrostatic forces between anions and cations due to the interaction of HBD with the quaternary salt leads to formation of a eutectic mixture in which both melting point and intrinsic viscosity are considerably lower than that of initial components. Owing to their promising properties, DESs have attracted widespread interest both at academic and industrial levels. Many publications have devoted to the use of DESs for the organic synthesis of catalysts, CO₂ absorbents, biodiesel purifying materials and other nanomaterials [28,29]. Based on some reports, using DESs in the synthesis medium enhances particle stability, weakens interactions between them and hence prevents agglomeration phenomenon. The main reason is that the ionic liquids exhibit high viscosity (due to the widespread hydrogen bonding network between their components leading to the restricted ion mobility) and high ionic strength (because of the high ionic density of their constituting molecules) [30]. Nonetheless, there are limited reports on the synthesis of inorganic materials in the presence of DESs.

In the present study synthesis of nano-CaP bioceramics in the presence of a deep eutectic solvent is discussed. ChCl–urea (CU) was employed as deep eutectic solvent and the precipitation process was performed under different synthesis temperatures. The effect of temperature on some characteristics of the synthesized CaP nanoparticles such as particle size, crystallinity and surface area was investigated.

2. Experimental

2.1. Materials

Calcium chloride anhydrous (CaCl₂, ≥ 98.0%), di-potassium hydrogen orthophosphate (K₂HPO₄, 98.0–100.5%), urea (CN₂H₄O, ≥ 99.0%) and Choline chloride (C₅H₁₄ClNO, 98.0–100.5%) were obtained from Merck company (Germany). All the chemicals were analytical grade and used without any further purification.

2.2. Preparation of deep eutectic solvent

The deep eutectic solvent was prepared by heating method according to Abbott et al. [31]. In a typical approach, ChCl and urea were mixed in a 1:2 M ratio, stirred and heated at 100 °C

until a homogenous liquid was formed. The resultant DES is designated as CU. A 1:2 M ratio of ChCl:urea was selected, because the resulting DES is liquid at room temperature. ChCl and urea could be mixed in 1:1 M ratio, however the resulting DES is not liquid at room temperature and has a melting point of 50 °C. Note that no eutectic solvent is formed at ratios lower than 1:1 or higher than 1:2.

2.3. Synthesis of CaP nanoparticles

In a typical synthesis procedure, 0.67 g CaCl₂ was dissolved in 50 mL CU deep eutectic solvent. Then a 0.81 M aqueous solution of K₂HPO₄ was prepared and rapidly poured into the calcium-containing solution until a gel-like suspension with Ca/P molar ratio of 1.5 was obtained. The formed suspension was kept under vigorous stirring for 20 min. It should be mentioned that different synthesis temperatures were examined: 25, 35, 55, 85, and 150 °C. The suspension was filtered, washed several times with deionized water (containing 0.001% v/v of 25% ammonia solution) and finally dried in a freeze-dryer (Pishtaz Equipment Engineering, DKLD-150-CAG) at –57 °C and 0.5 Torr pressure for 65 h. To prevent phase transformation, the dried CaP powder was immediately stored in a freezer. In order to investigate the effect of drying conditions on crystallinity of the precipitates, a sample was also synthesized in 25 °C according to above mentioned procedure except that it was finally dried in an oven at 60 °C for 24 h.

2.4. Characterization of CaP nanoparticles

Powder X-ray diffraction (XRD) patterns were taken by Siemens D-500 X-ray powder diffractometer with Cu-K_α radiation (λ = 1.5406 Å). The analysis was performed over an angular range of 2θ = 20–70° at a scan speed of 2 deg/min with step size of 0.02°. The crystallite size of some crystallized CaP samples was calculated using the Debye–Scherrer formula for (211) atomic plane (2θ = 31.9°) [32]

$$D_{hkl} = \frac{K \times \lambda}{\beta \times \cos \theta} \quad (1)$$

where D_{hkl} is average crystallite size, K is a shape factor, λ is the wavelength of Cu-K_α radiation, β is corrected broadening and θ is Bragg diffraction angle. In this formula, K was considered 0.9 for spherical particles and to remove the effect of instrumental broadening, β was corrected as follows [33]:

$$\beta = \sqrt{\beta_{exp}^2 - \beta_{standard}^2} \quad (2)$$

where β_{exp} is the measured width and $\beta_{standard}$ is the instrumental width produced by standard sample.

Morphology, particle size, and elemental image analysis of the CaP particles were investigated with a Tescan Mira 3 LMU field emission scanning electron microscope (FESEM) equipped with an energy dispersive spectroscopy (EDS) Quantax 200 (Bruker). The average diameter of CaP nanoparticles was estimated from FESEM micrographs using SemAfore software (version 5.21)

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