



One-pot and sustainable synthesis of nanocrystalline hydroxyapatite powders using deep eutectic solvents



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ABSTRACT

Nanocrystalline hydroxyapatite (HAp) powders were synthesized by a facile and sustainable method based on precipitation of calcium and phosphate reactants in choline chloride-urea deep eutectic solvent (DES). Characterization of the powders by X-ray diffraction, field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, and fourier transform infra-red spectroscopy revealed the formation of nanocrystalline HAp with average crystallite diameter of 33 nm, spherical morphology, Ca/P molar ratio of 1.64, and high elemental/structural purity. After synthesis, the DES was recovered successfully and re-used for the synthesis of HAp powders. Results on characterization of re-synthesized powders confirmed the synthesis of HAp nanocrystals with diameter of 30 nm, spherical to rod-like morphology, Ca/P molar ratio of 1.61, and high compositional purity. The findings of the present work endorsed the successful application of the DES as green, recoverable and affordable medium for the synthesis of nanocrystalline HAp.

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1. Introduction

Hydroxyapatite (HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) bioceramic is the most stable phase of calcium phosphate under physiological conditions, and one of the original components of hard tissues (e.g., tooth and bone) [1,2]. Among different structures of HAp, nanocrystalline HAp have gained a great deal of attentions in basic scientific research and biomedical applications due to its structural similarity to natural bone mineral [3,4]. Additionally, owing to their high surface energy and activity, and ultrafine structure, the nanocrystalline HAp exhibits enhanced resorbability, bioactivity, sinterability and densification. The superior properties led to the application of nanocrystalline HAp in different areas of biomedicine such as artificial bone, a drug carrier, cell imaging, and is biosensors [1,5].

The results show that the chemical composition, structure, biocompatibility, stability and properties of nanocrystalline HAp are greatly affected by the method of synthesis [6]. To days, several methods have been reported for synthesis of nanocrystalline HAp such as chemical precipitation [7], spray drying [8], sol-gel [9], mechanochemical method [10], hydrothermal [4], salvothermal [11], microemulsion [12], and wet chemical methods [13]. Synthesis methods of nanocrystalline HAp are usually done in the presence of surfactants and macromolecules to control the growth of

particles. The use of these substances leads to cytotoxicity of the nanocrystalline HAp and also imposes additional costs to the synthesis methods. On the other hand, simplicity, cost effectiveness, and eco-friendliness are of the major factors considered for the synthesis of nanomaterials [14]. Therefore, the adoption of a simple and green synthetic approach with the capability of control over the properties of HAp nanocrystals would be of great importance. Herein, a new and simple method based on using the new generation of green and environmental friendly solvents called deep eutectic solvents (DES) has been developed for the synthesis of nanocrystalline HAp powders. DESs are regarded as the green and cheap analogous of ionic liquids (ILs) that are formed through hydrogen bonding between two or three cheap and safe components [15]. In this work, the nanocrystalline HAp powders were synthesized in both fresh and recovered DESs and characterized by XRD, FESEM, EDS, and FTIR techniques.

2. Experimental

2.1. Materials

The analytical grade materials, Calcium chloride (CaCl_2), dipotassium hydrogen orthophosphate (K_2HPO_4), urea ($\text{CN}_2\text{H}_4\text{O}$), and Choline chloride (ChCl , $\text{C}_5\text{H}_{14}\text{ClNO}$) were obtained from Merck and applied without any purification.

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2.2. Preparation of deep eutectic solvent (DES)

Eutectic solvent used in this study was prepared according to the method provided by Abbott et al. [16]. Accordingly, 1 mol of choline chloride and 2 mol of urea were mixed together and then were heated at 90 °C for 1 h. After this time, a clear and viscous DES was formed.

2.3. Synthesis of nanocrystalline HAp powders

Nanocrystalline HAp powders were synthesized using a novel DES-assisted synthesis approach. In short, 1.5 g of CaCl_2 was dissolved in 100 mL of DES (ChCl-Urea) at temperature 150 °C while stirring on a magnetic stirrer with rate of 900 rpm. Then, a 1.62 M aqueous solution of K_2HPO_4 was added to the recent solution so that the ratio of Ca/P to be maintained at 1.67. Upon addition of K_2HPO_4 , a gel-like precipitate was emerged that gradually transformed into a milky and opaque precipitate. The resulting suspension was kept at 150 °C for 1 h under stirring at 900 rpm. After the time, the precipitates were filtered using a 0.2 μm filter paper, washed five times with deionized water and then dried in the vacuum oven at 60 °C for 8 h. The HAp precipitated accordingly was designated as f-HAp. In addition, to recover the DES solution, the filtrate was dried at 105 °C for 48 h and after filtration of the appeared crystal-like solids in the bottom of the pot, stored in a desiccator for 72 h. The recovered DES was re-used for the synthesis of HAp according to the latter procedure. The as-synthesized HAp was labeled as rec-HAp.

2.4. Characterization

The phase purity, crystallinity, and crystal size of the nanocrystalline HAp was analyzed by a Siemens d-500 X-ray powder diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Morphology and elemental image analysis of the nanocrystalline HAp were characterized by a Tescan Mira 3 LMU field emission scanning electron microscope (FESEM) equipped with an EDS Quantax 200 (Bruker) detector. The functional groups of the nanocrystalline HAp were determined by Fourier transform infra-red (FTIR) spectroscopy on a Perkin-Elmer Spectrum 400 instrument in the wavenumber range between 400 and 4000 cm^{-1} .

3. Results and discussion

Fig. 1 shows the XRD patterns of the synthesized f-HAp and rec-HAp powders. All diffraction peaks shown in the figure can be attributed to the well-crystalline HAp phase with hexagonal structure (JCPDS–9–432) [17]. The absence of any other peaks in XRD patterns is indicative of the high phase purity of the synthesized powders. The broad XRD diffraction peaks are indicative

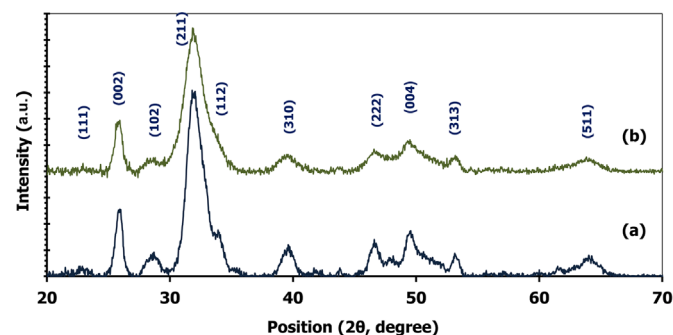


Fig. 1. XRD patterns of the as-synthesized HAp powders; f-HAp (a) and rec-HAp (b).

of nanocrystalline nature of as-synthesized HAp powders. Based on broadening of (002) peak, the average crystallite size of f-HAp and rec-HAp powders from Debye-Scherrer equation calculated to be 33 and 30 nm, respectively [18]. Based on Landy relation, the degree of crystallinity ($X_c\%$) for f-HAp and rec-HAp nanocrystals was found to be 94% and 86%, respectively [17]. The lower crystallinity of the rec-HAp compared to f-HAp can be explained in terms of both lower pH and viscosity of the recovered DES arising from the presence of some unreleased water molecules in its molecular structure (as confirmed by the FTIR analysis in the last Figure). The literature reveals that the supersaturation and pH of the solvent can highly affect the formation of HAp nuclei in solution. Nanosized crystals of HAp with the highest crystallinity are formed at higher pH values. Additionally, lower degree of supersaturation favors the formation of HAp crystals via higher conversion of amorphous calcium phosphate phase. The lower viscosity of the recovered DES decreases the interfacial surface area between the reactants, increases the level of supersaturation with respect to hydroxyapatite, and thus retards further conversion of amorphous phase into crystalline apatite. Thus, the lower pH together with the decreased viscosity of the recovered DES can result in low degree of crystallization in rec-HAp powders [19,20].

Fig. 2 shows FESEM and EDS patterns of as-synthesized HAp powders. FESEM micrographs reveal spherical agglomerates of nanoparticles with particle size generally smaller than 100 nm. Compared with f-HAp, the rec-HAp powders undergo further growth and some larger rod-like particles can be observed in the FESEM micrographs. This could be due to the decreased viscosity of recovered solvent resulted from unreleased fraction of water molecules in DES. According to the literatures, particle size and morphology are highly dependent of pH, interfacial tension and viscosity of the solvent [21–23]. The decreased viscosity of the recovered DES leads to increase of collisions between HAp nuclei during the synthesis and consequently, the formation of larger particles compared with fresh viscous DES. Also, lower viscosity of the recovered DES may increase the random collisions of the nuclei and further particle growth, which may result in HAp particles with a wide size distribution [21–23].

In order to demonstrate the elemental composition as well as purity of the samples, elemental image analysis was run on a larger surface area of the SEM image (The whole FESEM image area) of the samples. The provided EDS patterns in Fig. 2 show that both f-HAp and rec-HAp powders are composed of Ca, O, and P elements. No peak corresponding to other elemental impurities are seen in the patterns, suggesting the high purity of as-synthesized nanocrystalline powders. Semi-quantitative analysis using EDS data gives the average Ca/P ratios of 1.64 and 1.61 for f-HAp and rec-HAp powders, respectively. The obtained Ca/P ratios for the as-synthesized nanocrystalline powders are in good agreement with that of stoichiometric hydroxyapatite ($\text{Ca/P} = 1.67$) [4].

FTIR spectra of the nanocrystalline f-HAp and rec-HAp powders are shown in Fig. 3. Both samples show similar FTIR spectrum. The absorption bands at 471, 564, 603, 965, 1029, and 1111 cm^{-1} are related to the vibrational modes of tetrahedral phosphate ions (PO_4^{3-}). The bands at 631 and 3567 cm^{-1} could be indexed to the liberation and stretching vibration of hydroxyl group in HAp. The splitting of P–O asymmetric bending mode at 550–603 cm^{-1} further supports the crystallization of calcium phosphate as HAp as confirmed by XRD analysis [17]. The absorption bands detected at 1636 and 3431 cm^{-1} are devoted to the adsorbed water molecules. A small absorption band at $\sim 873 \text{ cm}^{-1}$ together with a peak split into two bands at 1462 and 1415 cm^{-1} are assigned to the carbonate group (CO_3^{2-}) which dissolved in the eutectic solvent and participated during the HAp formation to form carbonated apatite [2,17]. FTIR spectroscopy is considered as a reliable technique for

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