

Synthesis of morphology tuning multi mineral substituted apatite nanocrystals by novel natural deep eutectic solvents

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ABSTRACT

We report the fabrication of multi-mineral (Mg, Sr, Zn = MM) substituted apatite (HA) (MMHA) nanoparticles with different morphologies, which were successfully synthesized by a method based on precipitation of MMHA precursor in different natural deep eutectic solvents (NADES). Chemical structures were identified by FTIR, XRD and the crystal morphology was analyzed by SEM and TEM. The results reveal that the morphology of MMHA can be effectively controlled by the viscosity of NADES solvents.

1. Introduction

Hydroxyapatites [HA] are a principle inorganic components of human cartilages and teeth [1,2]. As well as multi-minerals substituted HA [MMHA] importance role in the biological activity of natural bones and teeth [3,4]. Synthetically produce MMHA are widely utilized in therapeutic areas such as orthopedics, orthodontics and medication release systems [5]. Furthermore, apatites with various morphologies have been employed in biomedical applications [6]. For instance, rod-like HA exhibits excellent adsorption ability because of their high specific surface region [5–7]. Spherical HA can be used as drug delivery due to its encapsulation and rescue capability and protein partition [8]. In addition, disc HA can be used an implant biomaterials because of its comparable structure to human bone [9]. Therefore, the morphology can substantially influence its features, for example, strength, viability, drug encapsulating prosperities, biocompatibility, etc [10]. Accordingly, plenty of surveys have been centered on the tunable synthesis of apatite with various morphologies [8–10]. The difficulty in controllable synthesis is the crystal augmentation [11], and it has been shown that templates play an important function in controlling the morphology development. This may be because the functional sections of the templates or solvents can lead to the nucleation and improvement of mineral crystals (MMHA) [12]. Earlier surveys have indicated that many compatible biomaterials, such as biopolymers, ionic liquids (ILs), and deep eutectic solvents (DESS) are often used for HA morphology controlling implements [13–15].

Establishing novel green solvents is one of the key subjects in Green Chemistry. Natural deep eutectic solvents (NADESs) were described initially by Duarte and co-workers [16]. They identified that hydrogen-

bond acceptor mixed (choline chloride) with hydrogen-bond donors of natural components such as sucrose, fructose, glucose and citric acid etc can form liquids at ambient temperatures. These liquids have characteristics analogous to those of deep eutectic solvents and ionic liquids namely, high conductivity, viscosity, surface tensions, polarity, and thermal stability and bio-compatibility [17]. Unlike ionic liquids, NADESs can still be simply produced as primary metabolites from available natural sources at a reasonable price and with great purity.

In contrast with conventional solvents such as water, ILs, DESS and NADESs form shielding layers around the precursor and produce both electrostatic and steric forces required to reduce the inter-particle synergies, growth regulation and phase stabilization of nanoparticles [18,19]. Therefore, the surface adsorbed natural component of the precursor plays an important part in precursor stabilization and managing the nucleation of apatite crystals by inhibiting the reaction of surface nucleation. Furthermore, NADESs have a small static dielectric constant, in contrast to conventional solvent like water. This promotes and speeds up the precipitation of stable nanoparticles due to the viscous, electrostatic repulsion of the NADESs solvent. In addition, in many cases, the solvent polarity may not be the only factor for morphology development of HA; other factors such as solvent viscosity, pH of the solvent and temperature may also affect the growth pattern of HA [6].

Furthermore, the anisotropic properties of apatite crystals have positive impacts on biocompatibility, bioactivity, and biodegradability [20]. In recent times, the biomineralization process of bone minerals has been accounted for in numerous research groups [6,20,21]. The HA crystals in normal bones do not originally nucleate within the depth regions, but certainly, a fluid-state amorphous precursor is brought into

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Table 1

Compositions, symbols, and molar ratios of the NADESs used in this study.

HBA	HBD	Add-on	Molar ratio	Symbol	Appearance	Viscosity (mPa s)
ChCl	Fructose	H ₂ O	5:2:5	NADES1 (ChCl-F)	Fairly viscous liquid	523
ChCl	Glucose	H ₂ O	5:2:5	NADES2 (ChCl-G)	Fairly viscous liquid	601
ChCl	Sucrose	H ₂ O	4:1:4	NADES3 (ChCl-S)	Fairly viscous liquid	866

the collagen fibers by capillary function, and the precursor crystallizes to HA crystals by applying metastable crystalline phases, for instance, octacalcium phosphate and brushite as transitory precursors [22].

Based on the importance and growth of HA crystals in normal bones, we inspect for the first time, the morphology of nano MMHA was completely governed by varying viscosity conditions in the synthetic method. The growth mechanism of MMHA with different morphologies confirmed their formation.

2. Experimental section

2.1. Materials and method

Commercially available $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , $(\text{NH}_4)_2\text{HPO}_4$, sucrose, fructose and glucose and $\text{C}_5\text{H}_{14}\text{ClNO}$ (ChCl) were brought from Aldrich Chemicals. First, both the hydrogen bond acceptor (ChCl) and donor (sucrose, fructose and glucose) molecules were heated at 80 °C with continuous sonication (SONICS vibracell) until homogenous and transparent viscous liquid NADESs were formed [16,17]. Table 1 illustrates the composition, molar ratios and symbols of the NADES used throughout this study.

In brief, 0.294 M Ca, 0.042 M Sr, 0.042 M Mg, and 0.042 M Zn was suspended in 50 mL of NADES1 (ChCl-F) and heated at 130 °C and sonicated for 10 min. Subsequently, 0.25 M $(\text{NH}_4)_2\text{HPO}_4$ aqueous solutions were included in the fresh solution so that the proportion of Ca (M)/P was maintained at 1.67. With the incorporation of $(\text{NH}_4)_2\text{HPO}_4$, a jelly-like residue appeared and slowly changed into a chalky and dense residue. The ensuing solution was set aside at 130 °C for 3 h under stirring at 1200 rev/min. Later, the residues of nanoparticles (MMHA) were extracted using Whatman filter paper, rinsed 6 times with double distilled water and afterwards desiccated in the vacuum oven at 50 °C for 5 h. The above process was established for other NADES2 and NADES3 ((ChCl-G) & (ChCl-S)) solvents.

2.2. Characterization

The presence of functional groups in MMHA nanoparticles were evaluated by Nicolet 380 FT-IR spectroscopy (Perkin Elmer, USA) within the scanning range of 4000–400 cm^{-1} and using a KBr pellet technique. The phases were characterized by XRD (PANalytical) with Cu K α radiation in the 2 θ range 20–60°.

The XPS spectra were obtained with SSX-100 spectrometer with monochromatized X-beam of Al K α radiation (1486.6 eV). The morphological characteristics and elemental constituents of the both MMHA nanoparticles were studied by FE-SEM (Curl Jdiss Supra 40–2007, Germany) operated at 10 kV accelerating energy, equipped with EDX. The microstructure of the nanocomposites was determined with high-resolution transmission electron microscopy (HRTEM) (HRTEM-JEOL JEM 2100 Co., Tokyo, Japan).

Samples for high-resolution transmission electron microscopy (HRTEM) examination were prepared by dispersing samples with ethyl alcohol, followed by sonication for 5 min. Subsequently, a droplet of the suspension was coated on top of a copper-deposited carbon grid with

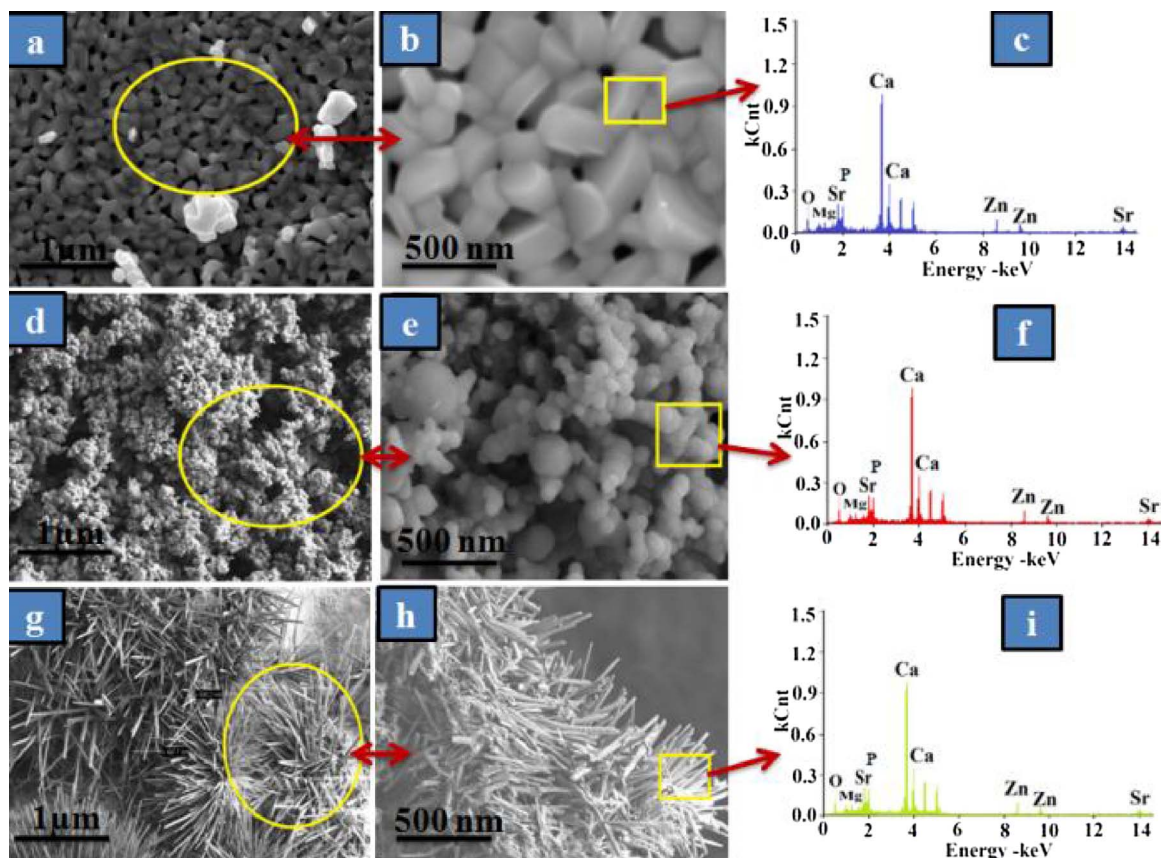


Fig. 1. FESEM-EDS images of the MMHA obtained at different NADES solvents, (a–c) NADES1, (d–f) NADES2, and (g–i) NADES3.

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