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Microwave-assisted synthesis of nanorod hydroxyapatite from eggshells

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Abstract:

Nanorod hydroxyapatite (HA) was synthesised from eggshells by using a microwave-assisted technique. With eggshells and phosphoric acid as precursors, the reaction was carried out in a microwave with an irradiation power of 800 W for 45 minutes. The effects of Ca/P molar ratios and the power of microwaves were investigated. The obtained hydroxyapatite was characterised by X-ray diffraction (XRD), scanning electron microscope (SEM), and infrared spectroscopy (IR). The nanorod-like HA samples were 20-40 nm in diameter and 130-180 nm in length.

Keywords: **eggshell, hydroxyapatite, microwave-assisted synthesis, nanorod.**

Classification number: **2.2**

Introduction

In recent years, hydroxyapatite [HA, $Ca_{10}(PO_4)_6(OH)_2$] has gained attention because it exhibits excellent biocompatibility with soft tissues, such as muscle, gums, and skin [1]. Moreover, HA is often used for bone grafting, orthopaedic and dental implants, or the components of implants. In addition, HA is also applied for the adsorption of heavy metal ions. This substance can be produced from fish scales, seashells, bodily fluids, natural calcite, and eggshells [2-8].

Every day, millions of tonnes of eggshells are generated around the world as bio-waste. The eggshell occupies about 11% of the total weight of an egg, and it consists of calcium carbonate (94%), calcium phosphate (1%), magnesium carbonate (1%), and organic matter (4%) (protein fibres) [3, 9]. Sometimes, eggshells are used as a fertiliser because of their high calcium and nitrogen content, as a foodstuff, or for animal use [3]. Due to high calcium carbonate content, eggshells can be used as a material for the synthesis of HA [6-8, 10, 11].

A number of synthetic methods have been used to prepare HA, including sol-gel, spray pyrolysis, as well as hydrothermal and chemical precipitation methods [7, 12]. The hydrothermal method is an effective and convenient way to synthesise HA with diverse controllable morphologies, such as nanospheres, as well as needle- and flower-like structures [4, 5, 11]. The preparation of HA from eggshells consists of two steps. Firstly, the eggshells are calcined to remove organic compounds and obtain calcium oxide. Secondly, the obtained calcium oxide is reacted with orthophosphate hydrothermally for conversion to HA. Then, HA nanostructures with different morphologies are prepared by using organic modifiers. However, the disadvantage of the hydrothermal method is that it is time consuming [13]. Therefore, a microwave-assisted technique can be used as a green energy and to save time for synthesis of HA.

Microwave irradiation is a simple method for the synthesis of HA due to its high reaction rate, time savings, rapid heating, and green energy [14, 15]. In this process, the size and shape of HA molecules can be controlled by the synthesis parameters [13, 15]. The purpose of this work is to prepare nanorod HA by microwave-assisted synthesis with the use of phosphoric acid, with eggshells serving as the calcium source. Furthermore, HA is a potential material for metal ion adsorption.

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Materials and methods

Materials

Eggshells were washed with boiling water to remove the membrane layer and dried overnight at 50°C in a box oven. After drying, the cleaned eggshells were ground into fine powder using a ball milling for 5 hours at 400 rpm. Phosphoric acid and ammonium hydroxide were purchased from Merck.

Methods

Preparation of hydroxyapatite from eggshells: the powdered eggshells were calcined at the temperatures of 800, 900, 1,000, and 1,100°C to convert $CaCO_3$ into CaO. Then, CaO (11.2 g) was dissolved in 400 ml of H_2O while being stirred for 1 hour at room temperature to obtain $Ca(OH)_2$ solution. Then, the solution was heated to 75°C. Subsequently, the phosphoric acid (0.3 M) was added to the solution with a dropper. The ratios of Ca/P were 1.65, 1.67, and 1.69. The pH of the solution was maintained between 10 and 12 by using ammonium hydroxide. After ultrasounding for 1 hour, the mixture was placed in a microwave reactor for a chemical reaction. The mixture was irradiated with microwaves at various powers of irradiation (300, 600, 800, and 1,000 W). The precipitate was washed to remove residuals and then dried in a box oven at 100°C for 6 hours to obtain the HA powders.

Characterisations of the decomposition of eggshells and HA: the chemical compositions of the eggshells were analysed with an X-ray fluorescence spectrometer (XRF) (S2 Ranger, Bruker, Germany). The crystalline phase of HA precipitates was investigated by X-ray diffraction (XRD) (D8 Phaser, Bruker, Germany) over a 2-theta (2θ) range from 10 to 60° with a scanning speed of 0.05°/min using CuKα radiation (λ=1.5406 Å) operating at the accelerating voltage of 40 kV and the current of 40 mA. The Joint Committee on Powder Diffraction Standards (JCPDS: 01-076-0694) was used for HA confirmation; HA formation was observed by Fourier transform infrared spectroscopy (FTIR) (FTS-3500, Bio-Rad, USA) using KBr pellets. The spectrum was scanned over 4,000-400 cm^{-1}. Surface morphology of the HA was observed using scanning electron microscopy (SEM) (JSM-6390LV, JEOL, Japan) at the accelerating voltage of 5 kV after gold coating.

Results and discussion

Effects of calcination temperature for the conversion of $CaCO_3$ into CaO

The chemical composition of eggshells depends on the calcination temperature. From the XRF results, after an increase in calcination temperature from 800 to 1,100°C for 4 hours, the percentage of CaO increased and reached the equilibrium value (95.6%) at 900°C. Therefore, the calcination temperature of 900°C was chosen for further experiments.

The effect of Ca/P molar ratios on HA formation

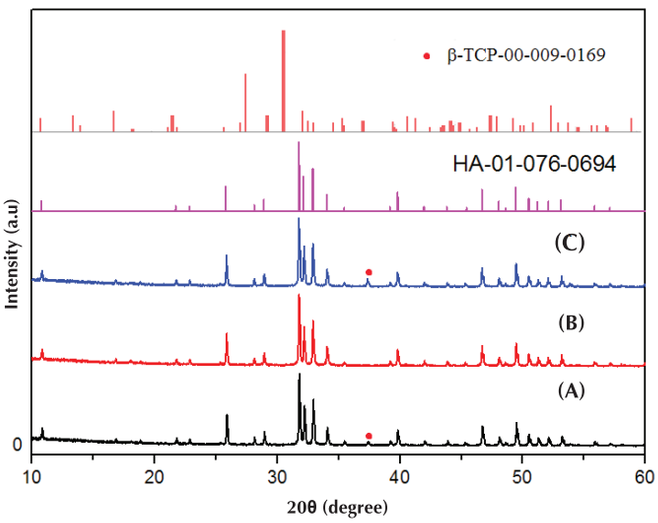


Fig. 1. XRD patterns of hydroxyapatite samples synthesised with the different molar ratios of Ca/P: (A) 1.65, (B) 1.67, and (C) 1.69.

Figure 1 illustrates the XRD patterns of hydroxyapatite samples with different molar ratios of Ca/P. The molar ratio of Ca/P was 1.67, and the characteristic HA peaks at 2θ angles of 25.89, 31.71, 34.06, 39.89, 46.73, 49.53, and 53.21°, corresponding to (002), (211), (202), and (301) Miller's planes, confirmed the formation of HA. No impurities peaks were found in the XRD pattern (Fig. 1B). In Fig. 1(A and C), the characteristic peak at 2θ=37.38° indicates the presence of β-TCP. Thus, the molar ratio of 1.67 for Ca/P was chosen for further experiments.

The effect of the power of microwave irradiation on HA formation

Figure 2 displays the XRD patterns of hydroxyapatite samples with different powers of microwave irradiation. With a power of microwave irradiation higher than 800 W, the characteristic peaks of HA were observed at 2θ angles of 25.90, 31.77, 32.15, 32.9, 34.04, 39.70, 46.68, 49.39, and 53.10°. All the peaks were indexed to hexagonal HA with no secondary phases, indicating that the HA was pure. The intensity of the highest peak was observed at a 2θ angle of 31.77°, corresponding to the (211) lattice plane, an increase from 80 to 800 W.

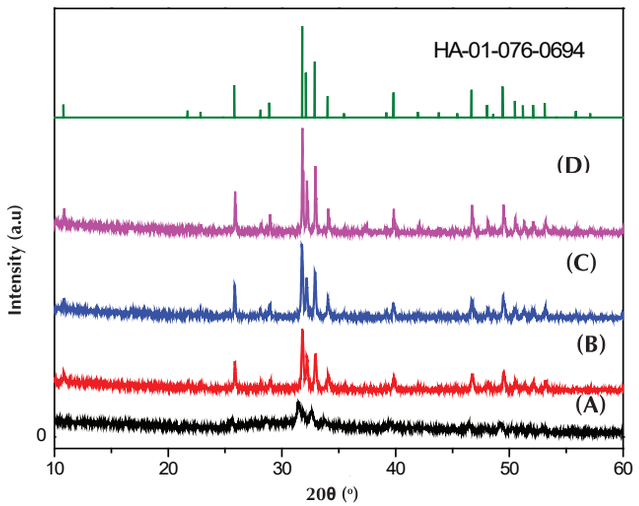


Fig. 2. XRD patterns of hydroxyapatite samples with the different powers of microwave irradiation: (A) 300 W, (B) 600 W, (C) 800 W, and (D) 1,000 W.

Figure 2C indicates that the highest intensity peak was at a 2θ angle of 31.78°. The average crystallite size (t) of HA was determined by the Scherrer equation:

$$t = \frac{0.9\lambda}{B\cos(\theta)}$$

where λ is the X-ray wavelength (λ = 1.5406 Å); θ is the diffraction angle; and B is determined by the "full width at half maximum intensity" located at 2θ. According to the Scherrer equation, the average crystallite size was 26.5 nm. This HA crystallite size is similar to the size of apatite crystals in previous studies [16].

Characteristics of HA

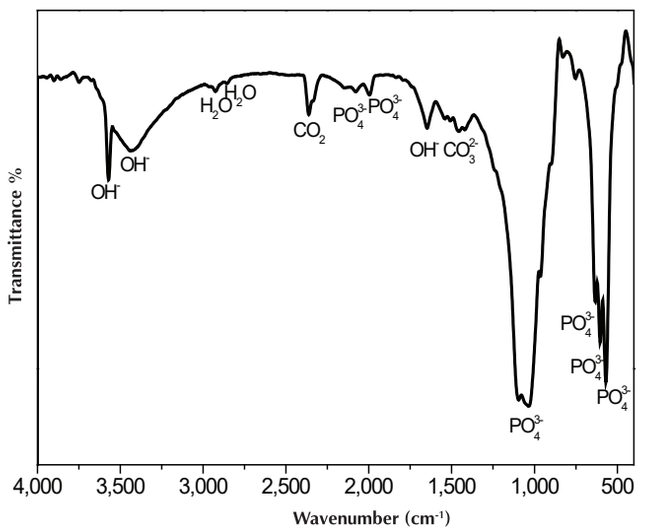
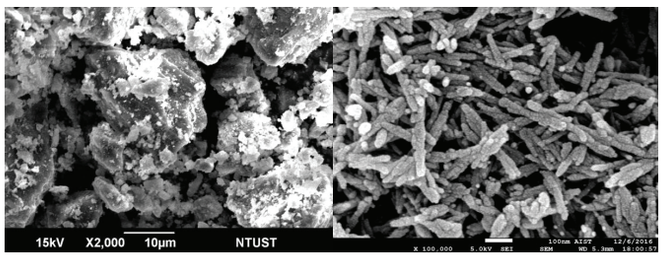


Fig. 3. FTIR spectrum of HA.

The FTIR spectrum of the synthesised HA sample is illustrated in Fig. 3. The characteristic peaks of functional groups of OH^- and PO_4^{3-} were observed in the IR spectrum. The characteristic peaks of the OH^- groups were at the wavelengths of 3,560 cm^{-1} (stretching mode) and 633 cm^{-1} (vibration). The characteristic peaks of the PO_4^{3-} groups were at the wavelengths of 565, 600 cm^{-1} (bending modes), 1,030 and 1,990 cm^{-1} (stretching mode) [17]. Moreover, a broad band observed at 1,630 cm^{-1} was attributed to the stretching modes of water molecules. The peaks of carbonate ions at 870 and 1,455 cm^{-1} were observed due to the substitution of the hydroxyl (-OH) and phosphate sites by the carbonate ions [17].



(A) (B)

Fig. 4. SEM images of eggshells (A) and hydroxyapatite sample (B).

Figure 4 contains SEM images of eggshells (Fig. 4A) and HA obtained after microwave-assisted synthesis (Fig. 4B). The eggshell powder was polyhedron. The polyhedron consisted of a multilayer of $CaCO_3$ (Fig. 4A). The HA obtained was uniform, and the morphology of HA was that of a nanorod of 20-40 nm in diameter and 130-180 nm in length. The nanorods of HA were obtained because the growth development of HA is along the c-axis due to its hexagonal symmetry [18]. Similar rod-like morphologies have been reported in previous studies [15, 19]. Besides, HA with flower- and sphere-like morphology has been synthesised by using microwave-assisted methods [9, 13, 14]. Thus, nanorod HA was successful prepared by using a microwave-assisted method in this research.

Conclusions

During this research, HA nanorods were successfully synthesised from eggshells and phosphoric acid as precursors using microwave-assisted technology. The temperature for the decomposition of calcium carbonate to form calcium oxide was 900°C. The uniform HA was obtained by applying a microwave irradiation power of 800 W for 45 minutes using XRD, IR, and SEM techniques. The HA produced had a nanorod-like morphology with samples of 20-40 nm in diameter and 130-180 nm in length.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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