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Conversion of waste eggshells to mesoporous hydroxyapatite nanoparticles with high surface area

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ABSTRACT

The objective of this work was to convert waste eggshells to mesoporous hydroxyapatite (HAp) with high surface area by using a simple and inexpensive protocol without complexes. The eggshells were initially dissolved in concentrated nitric acid under vigorous agitation to form $Ca(NO_3)_2$ solution, followed by the production of HAp nanoparticles through the addition of dilute phosphoric acid solution to the calcium solution at room temperature with a syringe pump. The HAp product possessed high surface area (212.4 m^2/g), large pore size (16.8 nm) and small particle size (<10 nm) as shown by BET and small angle XRD analyses. Moreover, only about 8% of the HAp phase was converted to whitlockite at high temperature (950 °C), indicating its stability.

1. Introduction

Hydroxyapatite (HAp) has gained much popularity in recent years due to its potential applications in several fields such as in bioceramic industry, medical and pharmaceutical areas and in environmental pollution control [1–3]. For applications in these and other areas, control of several parameters, including particle size, surface area, pore size, purity and morphology, is important as they dictate the properties of the HAp products [4]. Consequently, many techniques aimed at producing HAp that meets these and other properties have been explored [5]. For medical, pharmaceutical and bioceramic applications, HAp synthesized from biological calcium sources is preferred [6]. Accordingly, HAp synthesized from waste eggshells has been highly studied [7–10]. However, issues such as impurity, low surface area, poor thermal stability and larger particle size of the synthesized products have made the use of waste eggshells to generate HAp intended for the above fields almost unattractive [11]. To meet these quality issues, surfactants and structure directing agents, templates and in some cases complex procedures have generally been used [12,13], necessitating several purification steps. Calcium species for the syntheses of HAp from waste eggshells are obtained via several routes: dissolving the eggshells in concentrated acid [7], forming calcium complex [9] and converting the eggshells to CaO at high temperatures [8,10]. However, not much has been done towards improving the surface area or pore size of such biogenic HAp, although HAp powder with higher surface area and smaller particle sizes are reported to possess enhanced sinterability kinetics leading to enhanced properties [14] for diverse applications.

In this letter, we employed a simple procedure to synthesize mesoporous HAp nanoparticles directly from waste eggshells at room temperature. The objective was to convert eggshells into HAp with higher surface area (>200 m^2/g) and smaller particle size (<10 nm).

2. Experimental

Waste eggshells were collected from the Furong canteen in Xiamen University, China. Phosphoric acid (purity $\geq 85\%$), nitric acid (68%) and sodium hydroxide (purity $\geq 96\%$) were purchased from Sinopharm Reagent Co. Ltd, China. The eggshells were washed with detergent, then hexane and then distilled water, and dried at 80 °C overnight. The synthesis of HAp was achieved by dissolving the eggshells initially in concentrated nitric acid under vigorous agitation (800–1000 rpm) to control froth formation, at ambient condition through the reaction

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O \quad (1)$$

followed by the reaction (for 15 min) of 50 ml of 0.1 M of this calcium solution with 50 ml of 0.06 M of dilute phosphoric acid solution at an additional rate of 200 ml/h using a syringe pump (TCI-IV, China) while stirring (500 rpm) at ambient conditions. Note that the reaction was performed after pH of the $Ca(NO_3)_2$ solution was controlled to 10.4 by using NaOH solution according to

$$5Ca(NO_3)_2 + 3H_3PO_4 + H_2O \rightarrow Ca_5(PO_4)_3OH\downarrow + 10HNO_3 \quad (2)$$

The highlight of the procedure is the use of a syringe pump to control the addition of phosphoric acid, which facilitated effective

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control of the pH (9.8–10.4) of the reaction solution due to the consistency and precision of the addition rate. This ensured effective reactant dissolution, product formation and maturation over the addition period, resulting in the production of HAp with high surface area and pore size and small crystallite sizes [15]. The HAp products were washed with distilled water and vacuum dried at 70 °C overnight before subsequent heat treatments. The morphology of the products was studied by scanning electron microscopy (SEM; Hitachi). Thermal stability analysis was done with thermogravimetric analysis (TGA, Q600 TA), and specific surface area and pore volume were studied by BET (Micromeritics ASAP 2020, USA). X-ray diffraction (XRD, Rigaku Ultima IV) was performed to determine phase composition using a step size of 0.02° in 10 s counting range over 0.0–5° (for small angle) and 5–60° (for wide angle) in a reflection mode with CuK_{α} radiation.

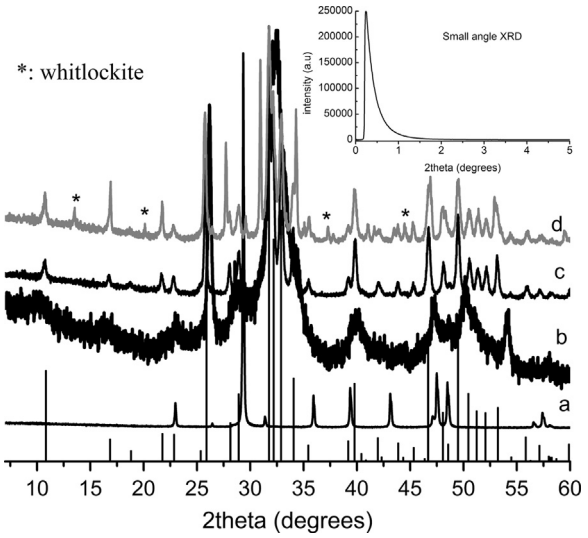

Fig. 1. XRD patterns for eggshells as the starting material (a), dried HAp product (b), and the calcined products at 700 °C (c) and 950 °C (d); bars: HAp reference (ICSD-PDF2: 01-074-0565); inset: small angle XRD indicating mesoporosity.

Meanwhile, the HAp structure was elaborated by Rietveld refinement with X'pert HighScore plus software and crystallite size was obtained using Jade 6.5 software.

3. Results and discussion

Fig. 1 shows the XRD patterns of the HAp products and the raw eggshells. The raw eggshells revealed respective calcite peaks corresponding to ICSD-PDF2: 01-083-0578 (Fig. 1a). The pattern of the dried HAp product revealed no impurity peaks; all peaks were indexed to hexagonal HAp (ICSD-PDF2: 01-074-0565) with P63/m space group and $a=b=9.3607$ Å, $c==6.7944$ Å, $v=515.5827$ Å^3 lattice parameters. The pattern also showed strong diffraction at 31.773° (Fig. 1b) in the 211 plane [8]. However, the peaks of patterns for the calcined samples (Fig. 1c and d) are stronger than those of the dried one (Fig. 1b), signaling better crystallinity due to the heat treatments. Additionally, the pure HAp phase was stable at 700 °C (Fig. 1c) but began to transform (≈ 8%) to whitlockite (ICSD-PDF2: 00-009-0169) phase at 950 °C (Fig. 1d).

Fig. 2 shows the SEM images of the raw eggshells, the HAp samples, and the calcined HAp samples. The raw eggshells possess highly agglomerated particles (Fig. 2a). The image of the particles from the dried sample had highly interconnected morphology (Fig. 2b). On heat treatments, this morphology was converted to porous particles at 700 °C (Fig. 2c) which subsequently densified into thick porous particles at 950 °C (Fig. 2d). Recall that bio-porous HAp ceramics are known to facilitate and enhance the circulation of body fluid when applied in metal coatings for implants and in surgery [16].

Table 1 shows the BET surface area and pore volume, and the crystallite size from XRD analysis. The powder had larger surface area and pore volume which is attributed to the small particle size and complex shape (Fig. 2b). A surface area of 212.4 m^2/g and pore volume of 0.98 cm^3/g were realized. These values are about the highest values documented for synthesized HAp by using waste eggshells without any templates or structure directing agents [17]. Moreover, the particle size obtained from the BET analysis was 8.9 nm which increased to 12.4 nm at 700 °C and to 53.7 nm at 950 °C. This was confirmed by crystallite size analysis from XRD

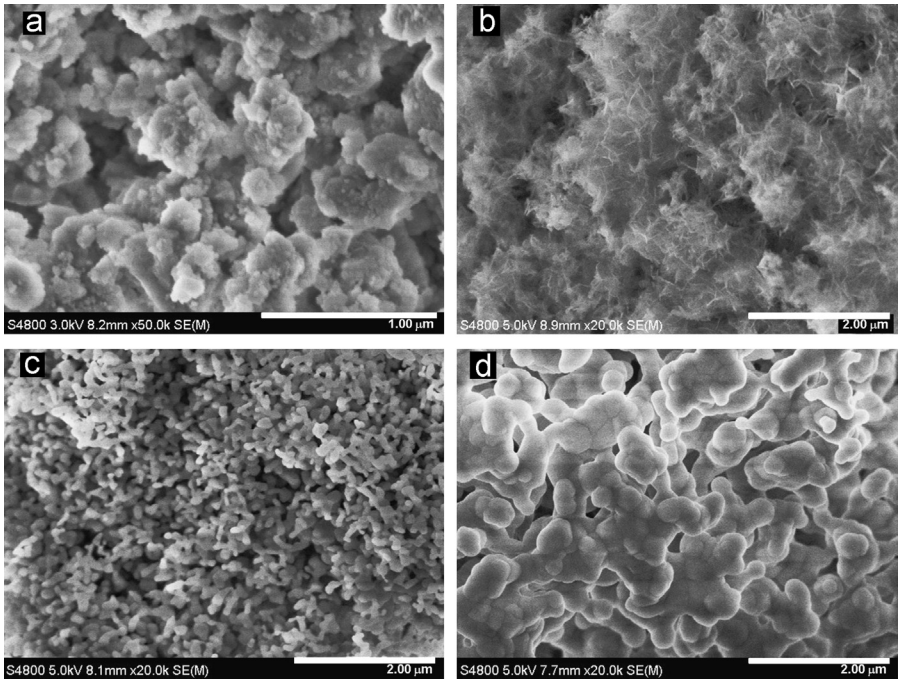

Fig. 2. SEM images of eggshells (a), dried HAp product (b), and the calcined products at 700 °C (c) and 950 °C (d).

Table 1
Results from BET and XRD analyses of the produced HAp powders.

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	APS[a] (nm)	ACS[b] (nm)
As-HAp	212.4	0.98	16.8	8.9	7
As-HAp 700 °C	153.1	0.43	11.5	12.4	12
As-HAp 950 °C	35.3	0.28	8.5	53.7	50

[a] Average particles size: obtained directly from BET analysis (density of HAp used was 3.17 g/cm^3).
[b] Average crystallite size: obtained from XRD using Jade 6.5 software.

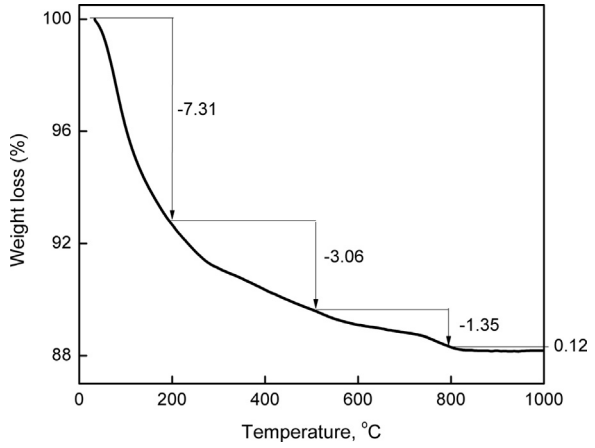

Fig. 3. TGA curve for the dried HAp sample produced at 200 ml/h.

patterns using Jade 6.5 software: 7 nm and 12 nm at 700 °C and 50 nm at 950 °C. Again, this is the first report on HAp obtained from eggshells with particle size lesser than 10 nm (Table 1). Even so, small angle XRD analysis (Fig. 1 inset) corroborated the smaller particle size and a further verification of the mesoporous nature of the product. Note that higher surface area biogenic HAp with highly interconnected nanoparticles will be useful in drug and drug delivery, and bone morphogenesis during bone surgery [3,18].

The thermal stability and weight loss of the produced HAp were studied by thermogravimetric analysis (TGA, Q600 TA) from ambient temperature to 1000 °C with a heating rate of 10 °C/min (Fig. 3). As can be seen, the product was relatively stable. The total weight loss was ≈11.8 % over the heating period. There was abrupt weight loss from ambient temperature to 200 °C resulting in a weight loss of ≈7.3 % and continued heating to 500 °C resulted in ≈3.1% weight loss. From 500 °C to 800 °C a weight loss of only 1.4% was witnessed, yet there was no appreciable weight loss from this temperature to 1000 °C, indicating the stability of the product.

4. Conclusions

This work reported conversion of waste eggshells to highly valuable hydroxyapatite nanoparticles with high surface area using a simple and inexpensive protocol without complexes. Mesoporous hydroxyapatite nanoparticles were produced at room temperature. The product had very small particle size (< 10 nm) and high surface area (212.4 m^2/g). Moreover, only about 8% of the HAp phase was converted to whitlockite phase at higher temperature (950 °C), indicating its stability.

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