JOURNAL OF MATERIALS SCIENCE **40** (2005) 5439–5442

Deagglomeration of HA during the precipitation synthesis

FENG XIAO*, JIANDONG YE, YINGJUN WANG, PINGGEN RAO
Department of Inorganic Materials, South China University of Technology, Guangzhou, 540641, China
E-mail: feng.xito@email.ucr.edu

Hydroxyapatite (HA) has been widely investigated as bone substitute and/or bone defect repairing material. Many methods to synthesize nano-sized and weak agglomerated HA powders have been developed. However, no method has a satisfactory balance between the powder quality and the production cost. In this study, a simple, cheap and efficient process to prepare nano-sized and weakly agglomerated HA powder was developed, in which ultrasonication and a polymer dispersant of PEG were employed. The synthesized powders were characterized with XRD, TEM, and BET specific surface area analyzer. The results showed that the cooperation of ultrasonication and polymer dispersant greatly weakened the agglomeration in the HA powders, but ultrasonication alone did not influence the agglomeration observably.

1. Introduction

Hydroxyapatite (HA), which is the major mineral composition of bone and teeth, has been used extensively in clinical applications as implants, bone defect fillers or coatings on prostheses [1]. Some of these applications require highly densified ceramic materials, which exhibit a high enough mechanical strength for load-bearing. Hydroxyapatite ceramics have excellent fatigue resistance if properly made without pores or second phases [2]. In this case, preparing a fine and sinterable hydroxyapatite powder is the first and perhaps the most important step in achieving this goal via conventional sintering at air pressure [3, 4]. Some other applications have involved composites of HA and polymer, such as Poly(alpha-hydroxyl acids) [5] and Polyethylene [6]. For these applications, homogeneous dispersion of HA particles in the polymer matrix is desirable. This requires the powder has a small average particle size and narrow particle size distribution and no hard agglomerates.

So far, a lot of work has been done in order to obtain nano-sized and weakly agglomerated HA powder, such as hydrothermal treatment [7] and microemulsion/inverse microemulsion route [8, 9]. Some of these methods can produce a high quality powder, but have a low cost efficiency because of its small batch production and/or expensive raw materials.

The precipitation process is the most reported method for preparing HA powder, which is simple, low cost and suitable for industrial production. But this method can easily lead to a low quality powder with a large particle size, wide particle size distribution and a lot of hard agglomerates [10]. In this work we report a precipitation process improved by the coordination of dispersant and ultrasonication to reduce the agglomeration in the HA powder.

2. Experiments

The HA powder was synthesized via the precipitation method at room temperature with $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ by titrating the stoichiometric amount of $(NH_4)_2HPO_4$ solution into $Ca(NO_3)_2$ solution (Fig. 1). The pH value of the reacting solution was kept at 10 with NH_4OH (pH=12). The reaction between $(NH_4)_2HPO_4$ and $Ca(NO_3)_2$ to form HA can be presented as follows:

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 \downarrow + 12NH_4NO_3 + 8HNO_3$$

In order to reduce the agglomeration during the precipitation, 0.3% sodium dedecyl sulfate (SDS) was added into the solution of $Ca(NO_3)_2$ as a dispersant before titrating. After titrating, keep stirring the reaction system for 24 h. The as-prepared precipitate was washed 5 times with distilled water and then twice with ethanol, followed by centrifuging for each washing step. The resulted gelatinous precipitate was dried at 70°C and then calcined at 700°C for 2 h to increase the crystallinity of the powder.

The preparation process stated above was improved by two methods: (i) method A: immediately after all the washing steps, ultrasonicating the precipitate in ethanol

---

[*] Author to whom all correspondence should be addressed.

0022-2461 © *2005 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-005-1919-6

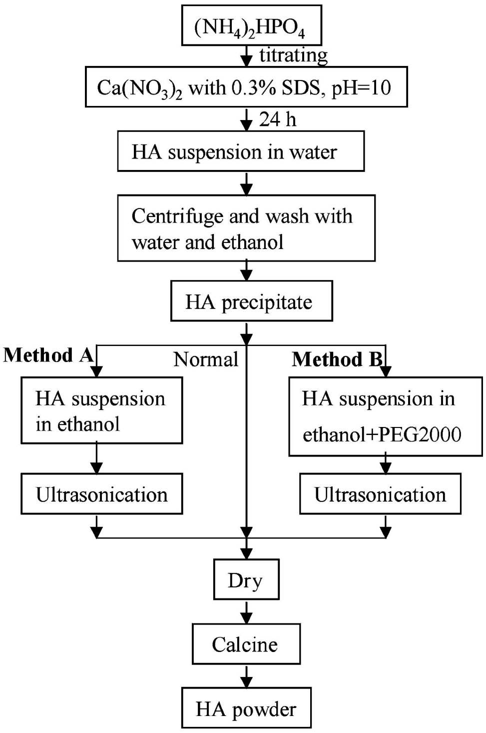

Figure 1 Process flow diagram of the synthesis of HA powder.

(precipitate: ethanol ≈ 1:2.5 by volume); (ii) method B: immediately after all the washing steps, 1 wt% (based on HA) polyethylene glycol ($M_W = 2000$, PEG2000) and ultrasonic agitation were at the same time introduced into the precipitate in ethanol (precipitate: ethanol ≈ 1:2.5 by volume). The ultrasonic power and frequency were arbitrarily fixed at 400 W and 28 KHz.

X-ray diffraction (XRD) (Cu K_α, Rigaku D(max-IIIA X-ray diffractometer) was used to analyze the phase compositions of the calcined and uncalcined powders. The crystal sizes d_{XRD} of the calcined powders were also calculated from the X-ray diffraction data. The particle sizes and morphologies of the powders were examined with a JEM-100CXII electron transmission microscope. Specific surface area measurements of the HA powders were carried out by BET nitrogen adsorption on a Coulter-SA 3100 surface area analyzer.

3. Results and discussion

Ultrasonication has been extensively used to disperse ceramic powders, which are usually hard-agglomerated. It is difficult to disperse the hard agglomerates by stirring or ball-milling. Ultrasonic agitation induces pressure waves in the slurry and thereby generates cavities in it. The cavities collapse violently to produce intense stresses, which can break particle agglomerates. In an earlier investigation, it was showed that there was a small effective range in the power/time used. Below the lower limit the dispersing was ineffective, but above the upper limit the ultrasonication caused the reagglomeration of particles [11].

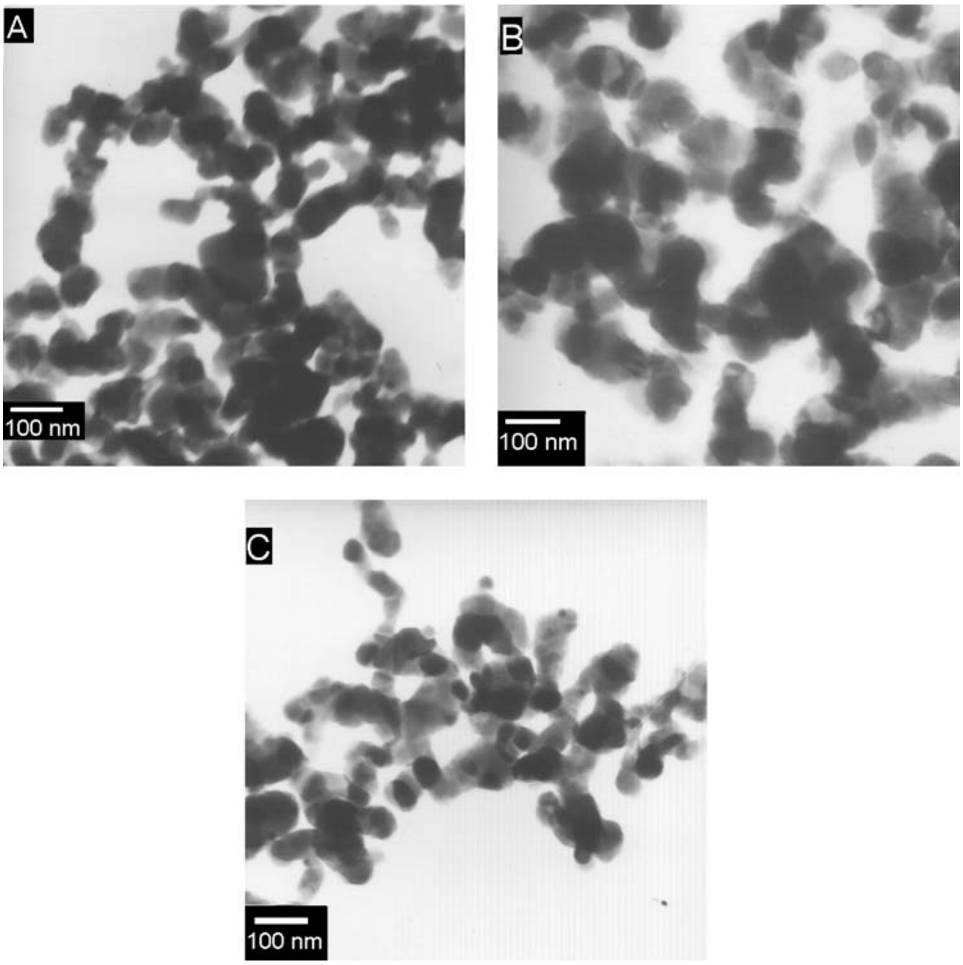

Figure 2 TEM micrographs of HA powder ultrasonication-treated for (A) 1.5 min, (B) 6 min, and (C) 60 min.

TABLE I S_{BET} and d_{XRD} of HA powder synthesized by the method A

Specimen	1	2	3	4
Ultrasonic duration (min)	0	1.5	6	60
S_{BET} (m^2/g)	21.47	26.99	32.05	22.94
d_{XRD} (nm)	30.27	30.83	30.84	28.69

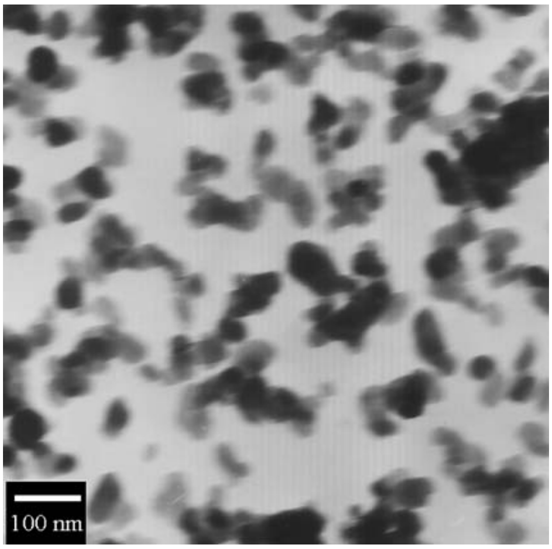

Figure 3 TEM micrographs of the specimen 5 synthesized with the method B.

Table I shows the results of the specific surface area S_{BET} and crystal size d_{XRD} for different ultrasonication durations. The specimens 1–4 were all prepared by the method A. The d_{XRD} represents the diameter of the primary particle or crystal size, calculated with Scherrer equation. All of the four specimens have approximately same values of d_{XRD}, indicating that ultrasonication seems not to obviously influence the size of the primary particles. So the S_{BET} can reflect the agglomeration situation of HA particles. The S_{BET} of specimen 1 is obviously smaller than the S_{BET} of specimen 3 and almost equals that of specimen 4. These results suggest that ultrasonication in a suitable dosage can obviously reduce the agglomerates of the nanoscale particles. But equilibrium seems to exist between the agglomeration and deagglomeration. When ultrasonic energy is applied, agglomerates can be broken into smaller particles. On the other hand, the smaller particles tend to form agglomerates so that reduce their high specific surface energy. When the two reverse processes have the same rate, the equilibrium is achieved. At this point, the maximum specific surface area can be obtained. However, because of this kind of equilibrium, highly dispersed powder is very difficult to obtain by ultrasonication alone. First, because it's not easy to determine the equilibrium point; second, even if the equilibrium is achieved, once ultrasonication is stopped the high specific surface energy will drive the fine particles to form agglomerates again. These agglomerates can become harder and even bigger during the later drying and heat treatment. This can explain why all the three specimens shown in Fig. 2 are badly dispersed.

To reduce the agglomerates, one of the most common ways is to add a dispersant, usually a kind of polymer surfactant, into the suspension. The polymer will be adsorbed onto the surface of the particles and form a thin layer of polymer, which can prevent the nanosized particles from forming agglomerates.

The specimen 5 was prepared with the method B. After washing of the precipitate, 1% PEG2000 was added into the suspension composed of ethanol and precipitates. The suspension was subject to 6 min's ultrasonic treatment. The resulted powder was dried and then calcined at 700°C for 2 hours.

Fig. 3 shows the TEM micrographs of the specimen 5. The particles of this specimen were dispersed better compared with those prepared by the method A. The specific surface area S_{BET} of the specimen 5 was 37.01 m^2/g. So the method B can greatly weaken the agglomeration of HA particles. Fig. 4 shows the

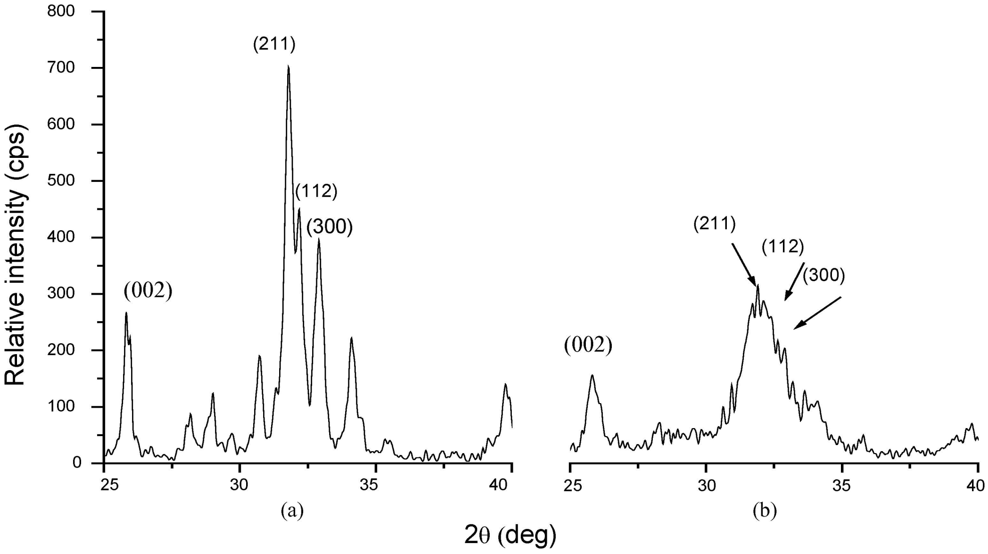

Figure 4 XRD patterns of HA powders: (a) calcined; (b) uncalcined.

XRD patterns of the powder calcined at 700°C and the uncalcined powder. The XRD patterns reveal that the powder without calcined is nearly amorphous. After calcination, the major diffraction peaks become sharp indicating the crystallinity of the powder has been increased.

4. Conclusion

The chemical precipitation synthesis of HA powder has been improved by the co-operation of ultrasonication and dispersant in this work. The synthesis is simple to employ and also has high cost efficiency. Ultrasonication can reduce the agglomerates of HA nanoparticles. But it is difficult to obtain a good dispersion by using ultrasonication alone because the dispersed particles will agglomerate again when ultrasonication is stoped. To obtain a better dispersion, the ultrasonication and dispersant should be combined. The molecules of polymer dispersant adsorbed on the surface of the HA particles prevent these particles from reagglomerating. Then, cooperatively with the dispercant, ultrasonication tends to only generate the effect of deagglomeration and greatly improves the dispersion of the powder.

Acknowledgements

This work was supported by NSFC Grants 50172015 and 59932050 and NSF of Guangdong Province of China Grant 011561.

References

1. L. L. HENCH, *J. Am. Ceram. Soc.* **74** (1991) 1487.
2. R. H. DOREMUS, *ibid.* **27** (1992) 285.
3. B. J. KELLETT and F. F. LANGE, *ibid.* **72** (1989) 725.
4. F. F. LANGE and B. J. KELLETT, *ibid.* **72** (1989) 735.
5. R. Y. ZHANG and P. X. MA, *J. Biomed. Mater. Res.* **44**(1999) 446.
6. M. WANG, D. PORTER and W. BONFIELD, *Bri. Ceram. Trans.* **93** (1994) 91.
7. Y. LI, et al., *J. Mater Sci: Mater. Med.* **5** (1994) 326.
8. G. K. LIM, et al., *Langmuir* **15** (1999) 7472.
9. *Idem., Mater. Lett.* **28** (1996) 431.
10. M. DE CAMPOS and A. H. BRESSIANI, *Bioceramics* **14** (2002) 171.
11. E. JORGE, T. CHARTIER and P. BOCH, *J. Am, Ceram. Soc.* **73** (1990) 2552.
12. T. S. SUZUKI, Y. SAKKA, K. NAKANO and K. HIRAGA, *Mater. Trans. Jim* **39**(1998) 689.

Received 9 January
and accepted 17 November 2004