Journal of Multidisciplinary Engineering Science and Technology (JMEST)
ISSN: 2458-9403
Vol. 7 Issue 5, May - 2020

A Brief Review On Hydroxyapatite (HA) Synthesis And Its Application

Bui Xuan Vuong
Faculty of pedagogy in natural sciences
Sai Gon University, Vietnam
Buixuanvuongsgu@gmail.com

***Abstract*—Hydroxyapatite (HA) has been widely studied because this material is similar to the inorganic component of human bone. HA material is proved to be biocompatible, bioactive, osteoconductive, non-toxic, noninflammatory, and non-immunogenic. With excellent properties, HA has been widely used in biomedical applications such as bone substitutes, implant coating, and bone filler. In the past fifty years, scientists have focused on the synthesis of this material with size, shape and morphology controls. In this review study, we provide readers with brief information on the synthesis method and the application of HA material.**

Keywords—Hydroxyapatite; synthesis; precipitation; structure, in vitro, and biomedical application

I. INTRODUCTION

Hydroxyapatite (HA) material is a class of calcium phosphates, which have been widely used as bone substitutes. In the past fifty years, HA material has been used for a variety of biomedical applications such as bone substitutes, implant coating, and bone filler. Because of the chemical composition similar to inorganic mineral of human bone, synthetic HA can strongly bond with the host tissue. Therefore, synthetic HA has a greater benefit in clinical application than most other bone grafts, such as natural allografts or alloy implants [1]. Due to brilliant properties, scientists have studied and synthesized the HA material by different ways, and have applied them as artificial bone materials. This paper presents the information on main methods for HA preparation and the application of this material in biomedical field.

II. SYNTHESIS OF HYDROXYAPATITE

A. Precipitation method

HA material has been widely synthesized by using chemical precipitation, in which chemical reactions occur between calcium and phosphorus ions in aqueous solutions under controlled conditions such as pH, temperature, stirring speed. The resulting precipitation is typically treated at temperatures in the range of 400 and 800 °C, to achieve a precise stoichiometric apatite composition. The precipitation method is a simple and un-expensive method, preparing HA material with characteristics similar to those of human bone. The purity, crystallinity, and morphology of synthetic HA are greatly dependent on the synthesis factors such as starting precursors, temperature, and time, addition rate of chemical reagent, aging step, and heating treatment [2-3]. A common reaction can be written as equation (1):

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 6H_2O \quad (1)$$

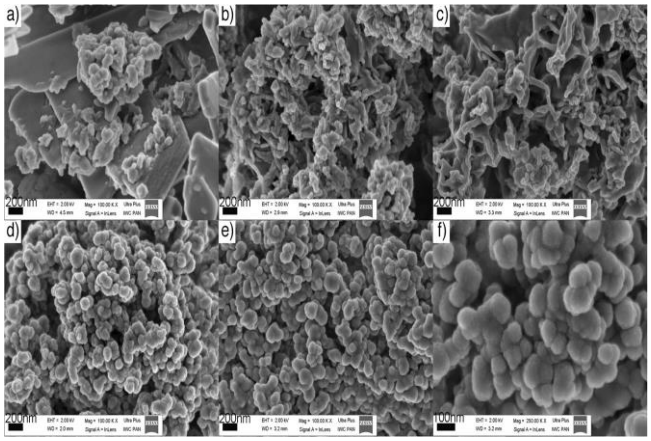

Fig. 1. SEM observations of HA powders synthesized using different amounts (% w/w) of lecithin a) 0.30 %; b 0.75 %; c) 1.50 %; d) 3.00; e) 9.00 %, and f) 9.00 %

Here, we presents a typical research, in which HA was synthesized by precipitation method using lecithin component as structural controlled agent. The authors indicated that different contents of lecithin results in changes of size, shape and morphology of obtained materials [4]. Fig. 1 regroups the SEM images of HA materials synthesized by precipitation method using different amounts of lecithin as structural controlled agent [4]. The observations shows that the size and shape morphologies of resulting

materials were dependent on the added amounts of lecithin.

B. Sol-gel method

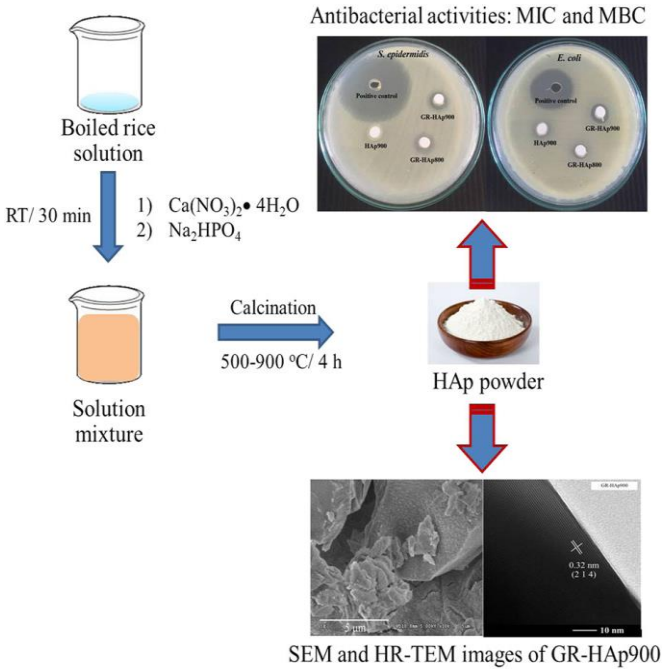

Fig. 2. Synthetic process and brief results in antibacterial application of HA material

Sol-gel method has been applied for more than 20 years for ceramic production. This process consists of two main steps. The first one is the dispersion of colloidal particles to form the sol. The second one is the gelation of sol particles to form 3D interconnected structure [5-6]. During the sol-gel processing, precursors (alkoxides) are mixed, stirred, aged, gelled, dried, and heated to organic removal. The synthetic materials have high purity and crystallinity due to the controlled parameters. Moreover, the obtained materials have homogeneous compositions and porous structures at low synthesis temperature [7]. The sol-gel method can use different chemical reagents to synthesize a wide range of structured materials with particle sizes in nano- and, or micro- scales [8-9]. In general, calcium nitrate is reacted with triethyl phosphate (TEP) in aqueous or organic solution. The chemical reaction can be presented as equation (2).

$$10Ca(NO_3)_2 + 6(C_2H_5O)_3P(O) \rightarrow Ca_{10}(PO_4)_6(OH)_2 + \text{residues} \quad (2)$$

In the sol-gel method, the conversion from sol to gel is usually accompanied by the agglomeration of particles due to the self-assembly phenomenon, resulting in an uneven distribution in the final structure. In very recent research, the authors have synthesize HA material by sol-gel method, in which glutinous rice (GR) was used as green template. The study shows that the use of GR resulted in formation of less crystalline materials with reduced agglomeration. Moreover, obtained HA powder shows good antibacterial effect [10]. The synthetic diagram and brief results in antibacterial application are presented in Fig. 2. The HA particles were successfully prepared by sol-gel technique using GR as a green template. SEM and TEM analyses confirmed the homogenous structure of obtained material. The in vitro test highlighted a good antibacterial effects.

C. Hydrothermal method

Hydrothermal synthesis is based on the chemical precipitation occurring at high temperature and pressure. The products can be quickly formed due to the energy of hydrothermal reaction. In this technique, organic compounds are usually used to modify and control the morphology and structure of obtained materials [11-12]. The hydrothermal reaction can be written as equation (3).

$$4Ca(OH)_2 + 6CaHPO_4.2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O \quad (3)$$

Here, we present a unique study on synthesis of HA material using hydrothermal technique [13]. Through reaction conditional control, the obtained materials showed different morphologies such as nano-rods, micro-spheres, hexagonal prisms, and hollow flowerlike structure (Fig. 3).

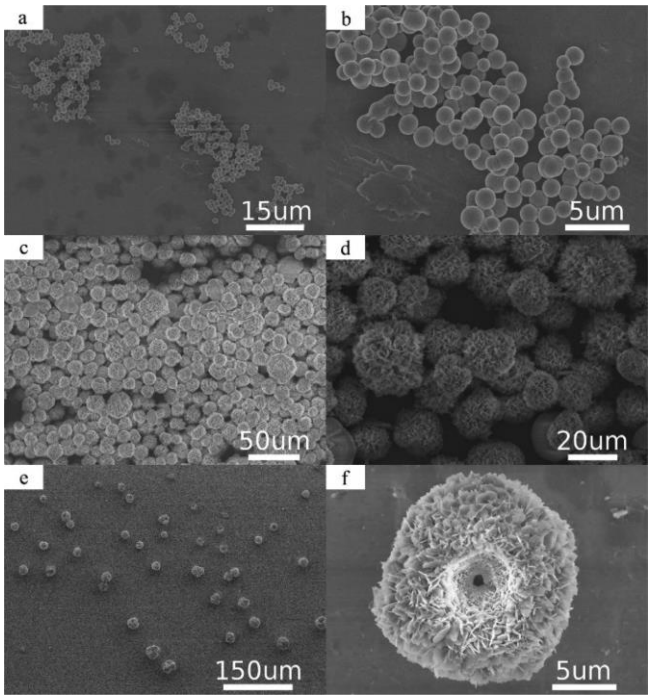

Fig. 3. FE-SEM observations with different morphologies of HA materials synthesized at different reaction times. (a, b) 40 min (c,d) 60 min, (e, f) 600 min

D. Other chemical methods for HA synthesis

Other chemical methods for HA synthesis have been reported such as the preparation of HA by microwave-assisted precipitation, which allows to achieve the rapid formation of hydroxyapatite in nano-structure; organic template –assisted electro-deposition to synthesize hydroxyapatite with nano-wires and nano-tubes; thermal plasma processing for synthesis of hydroxyapatite with nano-sizes [14].

E. Synthesis of HA from natural sources

Besides the synthetic methods used chemical reagents, HA material can be also efficiently synthesized from animal bones. Several scientists have prepared HA from bovine, caprine and galline bones by using thermal treatment at temperatures in range of 200 - 1200 °C. The study shows that the HA material from bovine bone was completely stable in the investigated temperatures while other extracted from caprine and galline bones expressed an in-stability by revealing tri-calcium phosphate (TCP) phase at the temperatures higher than 750°C [15]. The hydroxyapatite material with nano-rod shape (average length of 300 nm) was prepared by the heating process of bovine bone at the temperature of 750°C for 6 hours [16]. The HA powder was synthesized from fish bone by thermal treatment at temperatures from 100 °C to 1100 °C. The HA with high purity and crystallinity was obtained at a temperature of 800 °C [17]. The HA material was synthesized from porcine bone. The influences of temperature and sintering time on the structural property of HA were evaluated. The experiments showed an increase in crystalline degrees with sintering times [18].

In our study, HA material has been successfully extracted from pig bone by heating processing without any chemical treatment. The favorable condition for preparation of HA was determined as a heating raw powder at 750 °C for 6 hours. Moreover, the transformation of synthetic HA did not mention up to 1100°C [19]. Fig. 4 shows XRD diagrams of HA extracted from pig bone by heating samples at different temperatures for 6 hours. According to the HA standard (File JCPDS no. 09-432), the sample treated at temperature of 750 ^{o}C for 6 hours showed the high crystallinity compared to others.

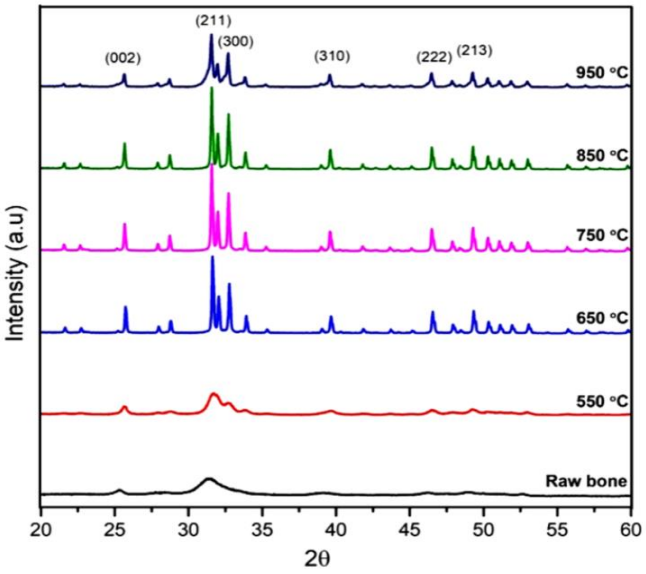

Fig. 4. XRD patterns of raw bone and bone treated at 550; 650; 750; 850 and 950 °C

III. VARIOUS APPLICATIONS OF HYDROXYAPATITE

Bio-ceramic HA have been widely used as bone replacement materials in biomedical applications such as bone tissue engineering; bone fillers for orthopedic, maxillofacial and dental surgery; orthopedic and dental implant coating; restoration of periodontal defects; fillers for reinforcing restorative glass ionomer cement (GIC) and restorative composite resin; mineralizing agent in toothpastes, and drug and gene delivery [20].

IV. CONCLUSION

This brief review essentially conveys the main methods for HA synthesis by chemical reactions and by extraction from natural sources. The typical references were selected to provide

readers with concise information on the synthetic processing, and the principal results. Finally, various applications of synthetic HA were presented in this brief review.

REFERENCES

[1] D.M. Liu, T. Troczynski, W.J. Tseng, Biomater. 22 (2001) 1721.

[2] E. Bouyer, F. Gitzhofer, M. Boulos, J. Mater. Sci. Mater. Med. 11 (2000) 523.

[3] Y. Pang, X. Bao, J. Eur. Ceram. Soc. 23 (2003) 1697.

[4] W. Michał, D. Ewa, C. Tomasz, Colloidal. Polym. Sci. 293 (2015) 1561.

[5] A. Siddharthan, S.K. Seshadri, T.S.S. Kumar, Scripta. Mater. 55 (2006) 175.

[6] A.S. Greenwald, S.D. Boden, V.M. Goldberg, J. Bone. Joint. Surg. Am. 83 (2001) 98.

[7] M.-F. Hsieh, L.-H. Perng, T.-S. Chin, H.-G. Perng, Biomater. 22 (2001) 2601.

[8] M. Houmard, Q. Fu, E. Saiz, A.P. Tomsia, J. Mater. Sci. Mater. Med. 23 (2012) 921.

[9] G.J. Owens, R.K. Singh, F. Foroutan, M. Alqaysi, C.-M. Han, C. Mahapatra, H.-W. Kim, J.C. Knowles, Prog. Mater. Sci. 77 (2016) 1.

[10] P. Phatai, C. M. Futalan, S. Kamonwannasit, P. Khemthong, J. Sol-Gel. Sci. Tech. 89 (2019) 764.

[11] Y. Qi, J. Shen, Q. Jiang, B. Jin, J. Chen, X. Zhang, Adv. Powder Technol. 26 (2015) 1041.

[12] Y. Wang, X. Ren, X. Ma, W. Su, Y. Zhang, X. Sun, X. Li, Cryst. Growth Des. 15 (2015) 1949.

[13] Y. Yang et al, Cryst. Growth. 14 (2014) 4864.

[14] M.P. Ferraz, F.J. Monteiro, C.M. Manuel, J. Appl. Biomater. Biomech. 2 (2004) 74.

[15] S. Ramesh et al, Ceram. Inter, 44 (2018) 10525.

[16] A.M. Nasser et al, J. Mater. Process. Tech. 209 (2009) 3408-3415, 2009.

[17] A. Pal et al, Mater. Lett. 203 (2017) 89.

[18] S. Ramesh et al, Ceram. Inter. 41 (2017) 10530.

[19] B.X. Vuong, T. H. Linh, J. Metal. Mater. Engin. 25 (2019) 47.

[20] D.S. Gomes et al, Ceram. 65 (2019) 282.

[21] S. Monika, Ceram. Inter. 41 (2015) 9203.