Bioengineering Research

Decreasing β-three Calcium Phosphate Particle Size Using Graphite as Nucleation Sites and Diethylene Glycol as a Chemical Additive

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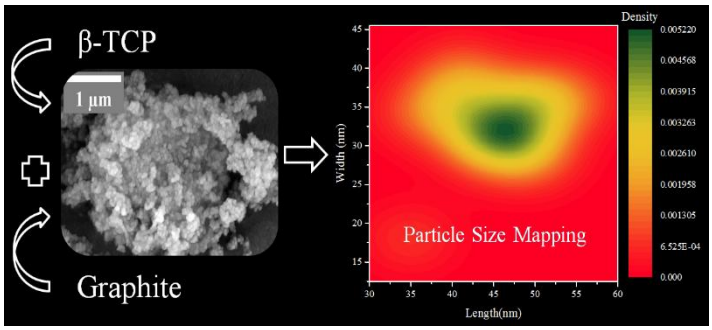
Abstract

Introduction: So far, several studies have been performed on nanosized β-TCP synthesis. In most of these studies, the results showed that the size of the synthesized particles was greater than 80 nm. Therefore, a change in process will be very useful if it results in a further reduction in particle size.
Objective: The main objective of this study is to synthesize uniform nano-sized β-TCP/graphite powders using diethylene glycol to decrease the particles size.
Material and Methods: The precipitation method was used in this study. The analysis performed in the sample includes X-ray diffraction, Field Emission Scanning Electron Microscope, X-ray photoelectron spectroscopy, and particle size mapping.
Result: The findings of this study showed that the synthesized powders are less than 60 nm x 45 nm. The interface between (002) planes in graphite and (214) planes in β-TCP are coherent. The three major peaks are responsible for crystal growth of β-TCP include (015), (220), and (214).
Conclusion: The powders synthesized in this research have the potential to be used in the medical applications.

Keywords: β-TCP; Graphite; Nanoparticles; Nanocomposites

Received: 10 December 2019, **Accepted**: 26 December 2019

DOI: 10.22034/jbr.2019.211371.1016



1. Introduction

Calcium phosphates have received much attention because of their similarity to the bone mineral. These bio-ceramics have unique properties such as biocompatibility, non-toxicity, and osteoconductivity [1-5]. Among the members of calcium phosphate family, hydroxyapatite (HA) and β-tricalcium phosphate (β-TCP) have received more attention than others. One of the disadvantages of HA is its insolubility in biological environment. However, β-TCP is more soluble than HA and has the potential to be widely used [6]. Nowadays, nanotechnology has improved materials properties by synthesizing nanoscale materials. In particular, chemical synthesis techniques such as sol-gel, hydrothermal, and precipitation methods, while leading to the synthesis of na nomaterials, have made it easier to control particle size and morphology. Particle size control in these methods can be accomplished by varying the pH, process temperature, process time, process pressure, ratio of the precursors, and chemical additives [7-9].

So far, several studies have been performed on nanosized β-TCP synthesis. In most of these studies, the results showed that the size of the synthesized particles was greater than 80 nm [10-13]. Therefore, a change in process will be very useful if it results in a further reduction in particle size. Among the various strategies available, the addition of nucleation and growth sites along with chemical additives like diethylene glycol (DEG) can modify the synthesis of smaller dimensions by changing the reactions kinetics. DEG (n=1) is one of several glycols derived from ethylene oxide. Ethylene glycole (EG, n=0) has been used as a reductant agent of GO. Also, Polyethylene glycol (PEG, n>4) has been used to decrease hydroxyapatite particle size and these compounds are all hydrophilic solvents [14-16]. These additives should maintain and even improve the unique properties of β-TCP. Among all the additives that have been added to calcium phosphates for various purposes, carbon nanomaterials have received more attention than others due to their good biocompatibility properties. These include carbon nanotubes, graphene, fluorine, and graphite [17-22].

Graphite is composed of graphene layers having hexagonal structure. The unique mechanical properties of graphene layers along with the good biocompatibility properties of these materials have recently attracted much attention. The graphene sheets spacing are highly correlated with the calcium phosphates crystal planes spacing. This makes the interface between the two phases coherent. Functional sheets need to be used for the process of calcium phosphate synthesis, like what exists on the surface of graphene oxide. In chemical methods, calcium ions first bond with agents present on the graphene surface. Then, phosphate ions bond with calcium ions and calcium phosphate nucleates and grows [23-28].

In this study, the precipitation method using calcium and phosphate precursors was used. X-ray diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), X-ray photoelectron spectroscopy (XPS), and particle size mapping were used to analyze the results. The results of this study could be useful for the medical applications of these powders [29-31].

2.Materials and methods

2.1.Powders synthesis

The primary chemicals used in the powders synthesis phase with the specifications are listed in Table 1.

Large-scale reduced graphite oxide was chemically synthesized from high purity flakey graphite. Graphite oxide was prepared by oxidation and exfoliation of graphite via the modifed Hummer's method. Stoichiometric amount of Calcium nitrate tetrahydrate and Diammonium hydrogenphosphate was dissolved in anhydrous ethanol and deionized water, respectively. First, the solution containing calcium ions was added dropwise to a 20 ml suspension of graphite oxide (4 mg/ml in DEG), which was stirring, and continued for an hour. Then, the solution containing phosphate ions was added dropwise to the previous set and finally the pH of the solutions was adjusted with ammonium solution. After that, the mixed solution was placed in an oven at 30°C. The precipitate was centrifuged, washed with deionized water and anhydrous ethanol several

times, and then dried in a vacuum oven at 80°C for 12 h. Finally, the dried powder was calcined at 800°C for 2 h in a vacuum furnace and employing a heating rate of 15°C/min.

2.2.Characterization

The characterization methods used in this study with the specifications are listed in Table 2.

Table 1: The primary chemical used in the powders synthesis phase

Chemical	Company	Purity	Formulation
Dyethylene glycol	Sigma Aldrich	99%	$(HOCH_2CHc)_2O$
Calcium nitrate tetrahydrate	Merck	> 99%	$Ca(NO_3)_2.4H_2O$
Diammonium hydrogenphosphate	Merck	> 99%	$(NH_4)_2HPO_4$
Ammonium solution	Merck	25%	NH_4OH
Anhydrous ethanol	Sigma Aldrich	> 99%	CH_3CH_2OH

Table 2: The characterization methods used in this study

Analysis Method	Instrument Specification
XRD	X' Pert Pro, Panalytical Co.
XPS	Thermo ESCALAB 250XI
Mapping	Origin Pro Software 2016
Modeling	Diamond Software 3.2
FESEM	Hitachi S4700 equipped with energy dispersive X-ray spectroscopy

3.Results and discussion

Figure 1 shows the Schematic picture of β-TCP crystal planes (a) and XRD pattern of β-TCP/Graphite powders (b). The X-ray spectra show that the peaks obtained are pure β-TCP. The three major peaks are responsible for crystal growth of β-TCP include (015), (220), and (214). The graphite sheets peaks in this spectrum are covered with β-TCP peaks. Consequently, it is clear that the calcium phosphate phase synthesized is all β-TCP [6].

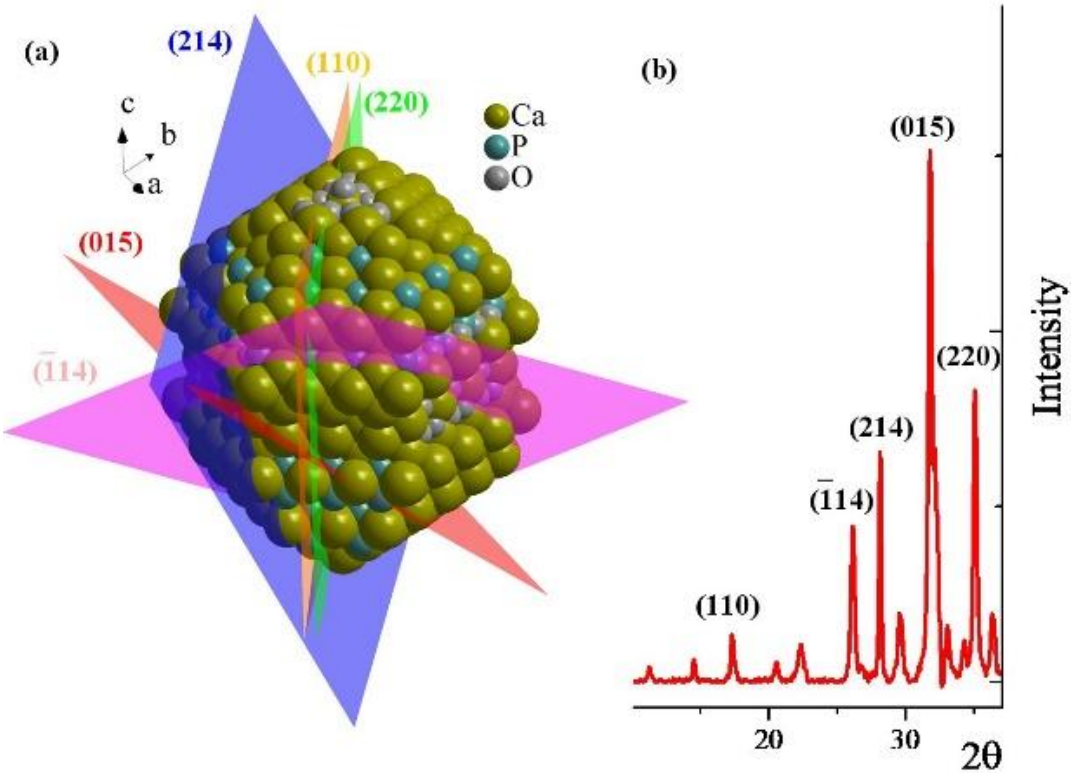


Figure 1. a) Schematic picture of β-TCP crystal planes, b) XRD pattern of β-TCP/Graphite powders

Figure 2 shows the schematic picture of interaction between β-TCP and graphite. (214) Planes distance and (-114) planes distance are very close to the graphene pales distance. However, since the (214) plane is more precise than the (-114) planes, a coherent interface is formed between the graphite cross-section, (002), and the (214) planes [23, 24].

Figure 3 shows the FESEM images of β-TCP/Graphite nano-powders at different magnifications. In Fig. 3a, the graphene sheets are folded out, and in the following images (Fig. 3b, Fig. 3c) it is clear that the synthesized particles are smaller than 100 nm. As can be seen in the images, the particles are stuck together and agglomerated and have a high density at the graphite cross-section.

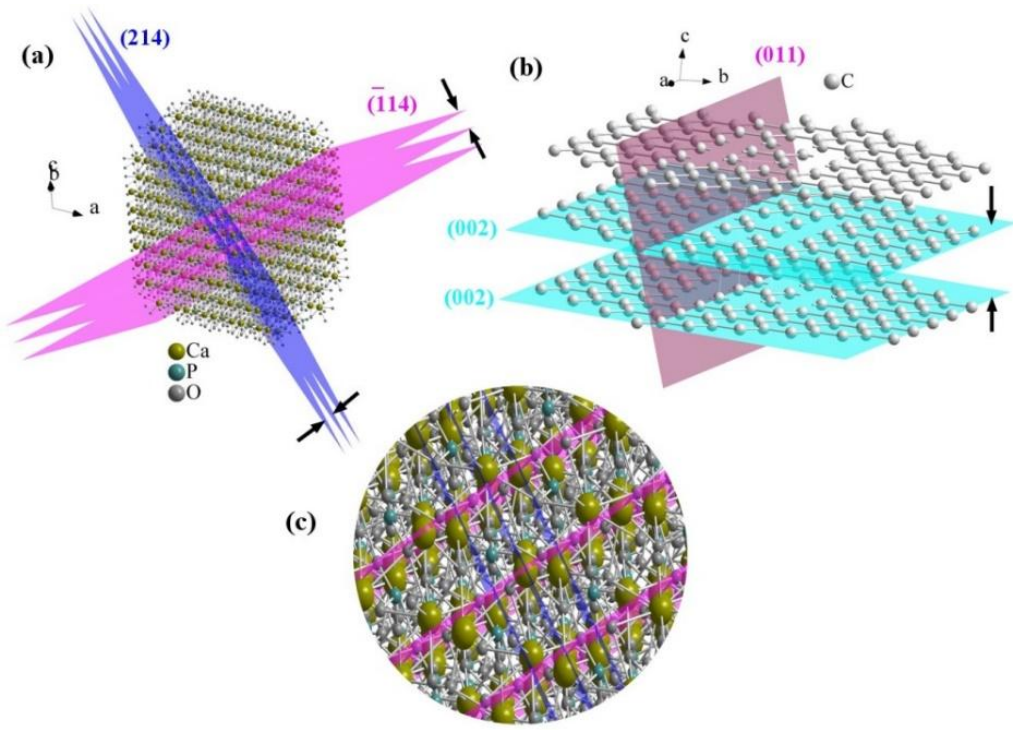


Figure 2. Schematic picture of interaction between β-TCP (a) and Graphite (b)

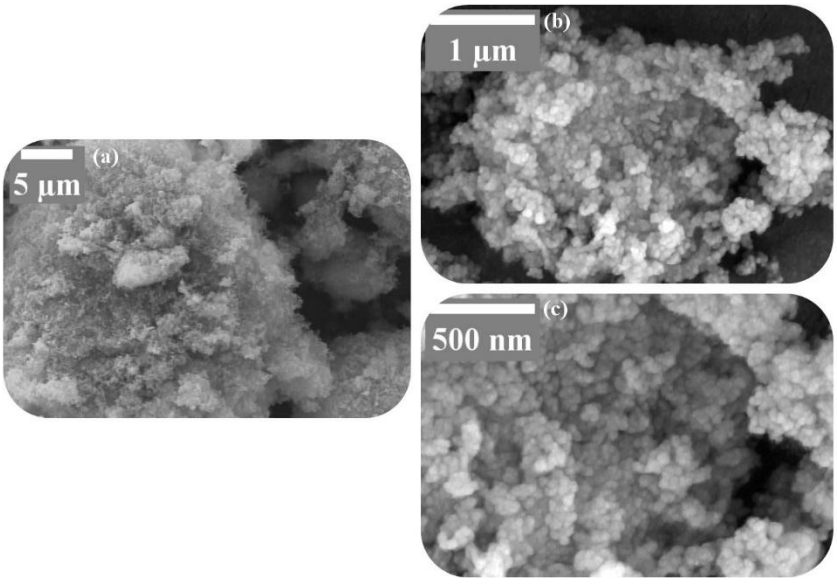


Figure 3. FESEM images of β-TCP/Graphite nano-powders

Figure 4 shows β-TCP Particle size mapping in 3D and 2D formats. The particles are known to have a length and width, and most of the particles (Density) are about 45 nm by 33 nm. But all particles are larger than 60 nm by 45 nm. The findings show that the particle size has decreased compared to previous research due to the effect of DEG on reaction kinetic. Diethylene glycol (DEG) can interact with calcium ions through ethylen oxygen groups in the molecules and mediate the size and morphology of β-TCP particles. At the same time, DEG can enwrap the precipitations and reduce the aggregation among the nano particles.

Figure 5 shows the EDS analysis and elemental mapping of β-TCP/Graphite nano-powders. These analyzes confirm the presence of trace elements and their homogeneity in the powders [23, 24].

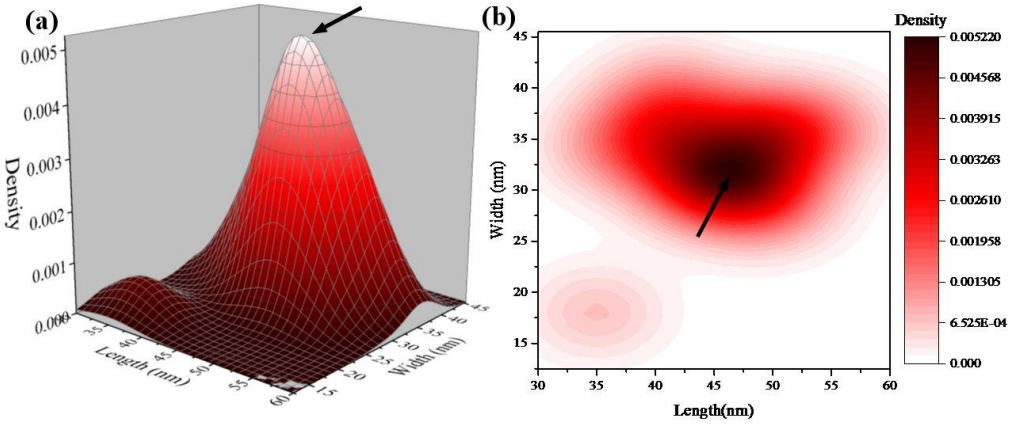


Figure 4. β-TCP Particle size mapping

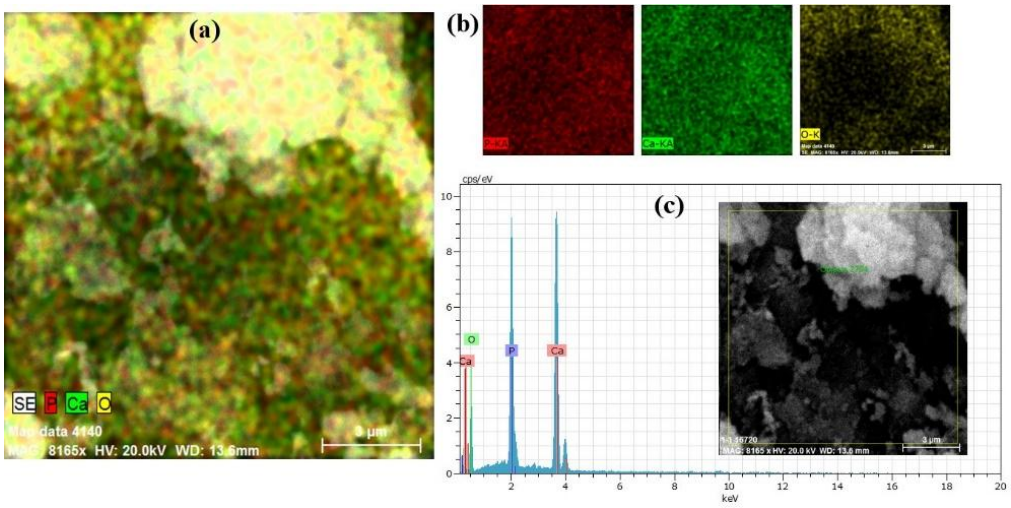


Figure 5. EDS analysis and elemental mapping of β-TCP/Graphite nano-powders

Figure 6 shows the XPS analysis of β-TCP/Graphite nano-powders. XPS is very useful to analyze the chemical composition of carbon materials. Fig. 6a shows the signals of Ca 2p and P 2p emerge in the XPS analysis of composites and confirms existing β-TCP and graphite. Fig. 6b shows that the oxide group remained similar to its graphite oxide counterpart because of strong electrostatic integration between oxide groups of graphite oxide and Ca2+ that prevents from reducing oxide groups of graphite oxide [23, 24].

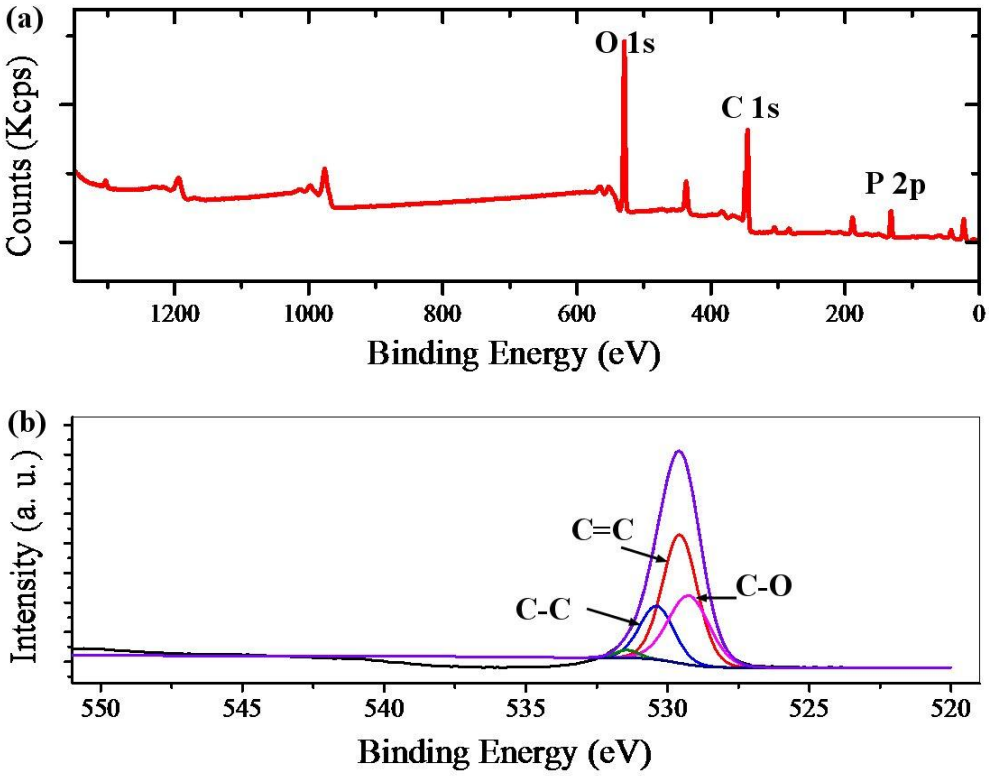


Figure 6. XPS analysis of β-TCP/Graphite nano-powders

Conclusions

The findings of this study showed that the synthesized powders are less than 60 nm x 45 nm. The decrease in particles size was due to the presence of diethylene glycol. The interface between (002) planes in graphite and (214) planes in β-TCP are coherent. The three major peaks are responsible for crystal growth of β-TCP include (015), (220), and (214). The XPS analysis confirmed existing β-TCP and graphite in the synthesized powders. The results of this study could be useful for the medical applications of these powders.

Conflicts of interest

The authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest, or non-financial interest in the subject matter or materials discussed in this manuscript.

Acknowledgments

No applicable.

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