



# Fabrication of porous hydroxyapatite-carbon nanotubes composite

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## ARTICLE INFO

### Article history:

Received 26 September 2015

Received in revised form

16 October 2015

Accepted 27 December 2015

Available online 29 December 2015

### Keywords:

Biomaterials

MWCNTs

Biocomposites

Scaffolds

Porous materials

Adsorption

## ABSTRACT

Porous hydroxyapatite (HA)/carbon nanotubes (CNTs) composites were produced by using polymeric sponge route through double firing method (500 °C for 0.5 h and 1000 °C for 1 h). HA nano crystals were synthesized by the hydrothermal method at 200 °C for 2 h and mixed with aqueous CNTs suspension. For the functionalization of CNTs, acidic treatment was used. Polyvinyl Alcohol (PVA) was used as a binder for the formation process of HA/CNTs composite ceramics. Addition of CNTs can enhance its mechanical, biological and filtration performance of the porous HA/CNTs composite ceramics. The novelty of this paper relies on the fabrication of the HA/CNTs composites have been accomplished with tailored pore structure. The research shows that developed new technique is able to design and control pore structure of ceramic/CNTs composite for potential use in biomedical and environmental applications.

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## 1. Introduction

Porous hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (HA), is one of the ceramic materials for biomedical and environmental applications due to its unique biocompatibility and adsorption property [1–3]. Pores size and morphology of the bioceramics play an important role in the biological fixation and mechanical bonding of bioceramics to bony tissues. Despite fixation and bonding ability, the mechanical strength of the bioceramics decrease by the increasing pore content. Therefore, the porous-structured HA possesses lower mechanical performance than other dense HA ceramics. Some of reinforcement materials such as  $\text{ZrO}_2$  [4],  $\text{Al}_2\text{O}_3$  [5], SiC [6],  $\text{Y}_2\text{O}_3$  [7],  $\text{TiO}_2$  [8] and CNTs [9–14] have been used to improve the mechanical properties of HA. CNTs are hollow tube-shaped structures made up of one-atom-thick layers of hexagonal patterned graphene sheets rolled up, with all the carbon atoms forming three bonds at a time with each other through  $\text{sp}^2$  hybridization. CNTs are one of the extremely strong reinforcement material for improving the mechanical performance of the composite materials because of their superior properties. Besides owing to CNTs' chemical properties, they are able to adsorb biological and chemical contaminant.

There are many techniques used in the production of porous materials. These are slip casting [15–18], gel casting [19–23], starch consolidation [24], gas foaming [25,26], freeze casting [27,28], electrophoretic deposition [29,30], 3D printing [31] and polymeric sponge [32–35]. Polymeric sponge technique is cost effective technique compared to other techniques and that provides control of the pore morphology.

In this study, HA with porous/multi wall carbon nanotubes

(MWCNTs) composite ceramic have been shaped through polymeric sponge technique and produced by using a two-step heat treatment. Enabling the fabrication of the tailored porous HA/MWCNTs was shown in the present work by means of new technique. The produced porous ceramics could be used in biomedical and environmental industry with its controllable pore structure, biological properties and potential to adsorb such as heavy metals, and biological waste.

## 2. Experimental

Porous HA/CNTs composite were produced using polymeric sponge route as a novel fabrication technique. To obtain HA, Calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ , Merck KGaA, Darmstadt, Germany) 94.64 g was dissolved in 400 ml in distilled water and to maintain the pH of the mixture above 10, ammonia solution (28%, Merck Co. Darmstadt, Germany) were used. Ammonium dihydrogen phosphate ( $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ , Merck KGaA, Darmstadt, Germany) 31.72 g was dissolved in 400 ml distilled water and the pH of the solution was adjusted to 10 with addition of the ammonia solution. Ammonium dihydrogen phosphate solution was added drop by drop to calcium nitrate tetrahydrate solution at the same time stirred with a magnetic stirrer. The resulting product is denoted as precipitated HA. The precipitate was poured in a Teflon-lined stainless steel vessel. The sealed vessel was kept in an oven at 200 °C for 2 h for the hydrothermal treatment. After hydrothermal treatment the reaction product washed with distilled water and denoted hydrothermal HA.

For the preparation of HA/MWCNTs suspension, solid material

concentration of the suspension was adjusted 40 wt% and acid modified ( $\text{HNO}_3/\text{H}_2\text{SO}_4$ , 1/3) MWCNTs' (Shenzen Nanotechnology Co Ltd., China) concentration was kept 2 wt% in the suspension. The suspension was mixed with a magnetic stirrer for 2 h. and ultrasonicated for 10 min. The organic binder Poly vinyl alcohol (PVA) was added to the resultant mixture. Concentration of PVA was 2 wt% of solid matter content in suspension. Then, commercial polymeric sponge templates were immersed for 2 min. in HA/MWCNTs suspension and subsequently, dried at room temperature for 48 h. A tube furnace (Protherm PTF 15/50/250, Turkey) was used for the burn-out of polymer sponge and the binder. Burn-out took place at an ambient atmosphere at 500 °C for 30 min. with a heating rate of 2 °C/min to avoid cracking during the burning-out of the polymeric sponge. And then burned-out composites were gently transferred to a vacuum furnace (Gero LHTG 200–300) to prevent burn-out of CNTs and sintered from room temperature to 1000 °C at a heating rate of 2 °C/min. and maintained at 1000 °C for 60 min. to produce porous HA/MWCNTs composite.

The synthesized products were characterized by transmission electron microscopy (TEM, JEOL 2100 HRTEM). For the phase characterization of the synthesized HA nano crystals, X-ray diffractometer (XRD, Rigaku, RINT 2200 VL) were used with  $\text{CuK}\alpha$  radiation. Thermogravimetric analysis (TGA) was performed in a Pt crucible (TA SDT Q600) at a heating rate of 10 °C/min in a dry air flow to determine the burning-out of polymer sponge, PVA, and MWCNTs. A microstructural evaluation of the sintered porous HA/MWCNTs bioceramic was conducted by scanning electron microscopy (SEM, JEOL JSM-7000F).

### 3. Results and discussions

The TEM photographs of the synthesized nano crystals were shown in Fig. 1. After the precipitation process of HA, the obtained nanocrystals exhibit irregular morphology. On the other hand, HA nano crystals were transformed into needle-like regular shaped crystals by the hydrothermal treatment. According to TEM images, the crystal size and morphology of HA nanocrystals were improved, by the hydrothermal process due to dissolution–recrystallization phenomena and accelerated formation of HA reaction. After the hydrothermal treatment the synthesized remaining nano crystals have well-defined sizes. Hydrothermally synthesized HA nano crystals are approximately two times bigger than precipitate HA nano crystals (Table 1).

X-ray diffraction (XRD) patterns of precipitated HA and hydrothermal treated HA, are shown in Fig. 2. All the peaks correspond to stoichiometric HA (JSPDS Card no. 09-432). And there is no peak indicating the presence of anhydrous calcium phosphate.

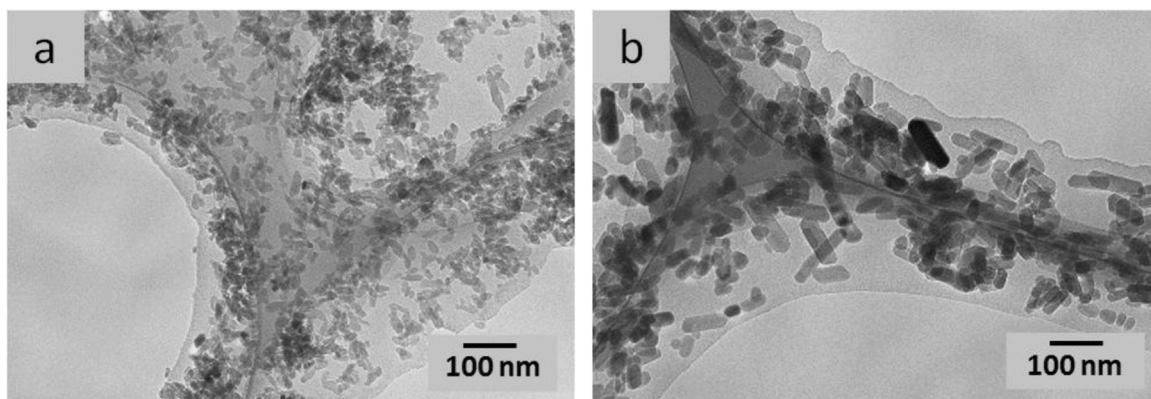


Fig. 1. TEM images of precipitated HA (a) and hydrothermal HA at 200 °C for 2 h (b).

Table 1

Summary of the crystallinity and crystal size change of the synthesized HA nano crystals (According to TEM and XRD observations).

Sample	Width (nm)	Length (nm)	Intensity of (211) plane (cps)
Precipitated HA	11.70 ± 4.16	24.64 ± 10.73	328
Hydrothermal HA	23.25 ± 4.02	49.33 ± 21.14	545

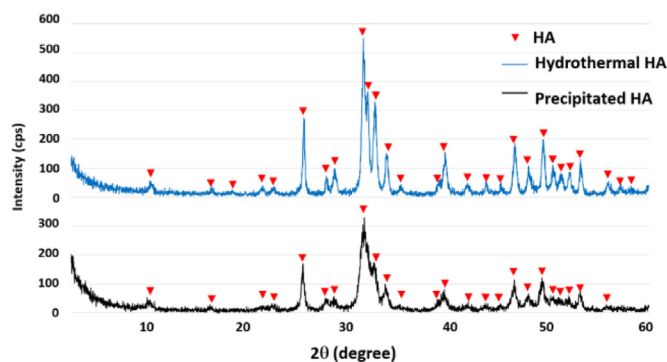


Fig. 2. XRD pattern of the synthesized HA nano crystals (JSPDS Card no. 09-432).

XRD studies show that after the hydrothermal treatment, there is an increase in crystallinity. XRD peaks of the HA nano crystals became sharper and the intensity of XRD peaks increased with hydrothermal process, which means that crystallinity and morphology are enhanced by the hydrothermal treatment.

To determine the thermal stability of polymeric sponge, PVA, and MWCNTs thermogravimetric analysis was performed. TGA results were shown in Fig. 3. TGA experiments indicated that the decomposition of polymeric sponge started at 230 °C and finished at 345 °C. PVA was burned-out at 480 °C in two steps, dehydroxylation and polyene decomposition steps, respectively. According to TGA results, MWCNTs begin to oxidize at 550 °C and the reaction completes at 725 °C. Therefore, the burn-out temperature of the HA/MWCNTs was chosen 500 °C. At this temperature range polymeric sponge and PVA removes from the material, but at the same time MWCNTs remain intact. Preservation of MWCNTs in the structure is believed to enhance mechanical and adsorptive properties of the porous composite. Polymeric sponge was used as a template for formation process, and shaped materials might collapse due to polymeric sponge combustion during the burn-out process. Therefore, burning-out heating rate was performed at 2 °C/min to prevent the deformation of porous composite and micro crack formation.

Microstructure analysis of the sintered porous HA/MWCNTs

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