Materials Letters 169 (2016) 24–27

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Development of functionalized carbon nanotube reinforced hydroxyapatite magnetic nanocomposites

J.D. Afroze [a,c], M.J. Abden [b,c,*], M.S. Alam [a], N.M. Bahadur [a], M.A. Gafur [c]

[a] Department of Applied Chemistry and Chemical Engineering, Noakhali Science and Technology University, Noakhali 3814, Bangladesh
[b] Department of Electrical and Electronic Engineering, International Islamic University Chittagong, Chittagong 4203, Bangladesh
[c] Development of Materials for Tools and Bio-Metallic Implant, Bangladesh Council of Science and Industrial Research, Dhaka 1205, Bangladesh

ARTICLE INFO

Article history:
Received 20 October 2015
Received in revised form
29 December 2015
Accepted 16 January 2016
Available online 16 January 2016

Keywords:
Hydroxyapatite
Carbon nanotubes
In-situ fabrication
Nanocomposites
Magnetic properties

ABSTRACT

An innovative and effective approach is introduced to functionalize multi-walled carbon nanotubes (f-MWCNTs) by in-situ chemical precipitation of hydroxyapatite (HA) to improve their magnetic properties. The HA/f-MWCNTs nanocomposites are obtained by pressureless sintering in vacuum atmosphere. The carboxyl functional group (–COOH) is introduced by an acid treatment on the MWCNT surface. Magnetic hysteresis measurement reveals that HA/f-MWCNTs nanocomposites exhibit excellent hard ferromagnetic properties with saturation magnetization (M_S) of 0.233 emu/g and coercivity (H_C) of 2985.53 Oe at room temperature. The maximum magnetic hysteresis loss of 0.44 kJ/m^3 induces an expected heat generation and it is expected that this nanocomposite has potential to be used as a biomaterial for hyperthermia treatment of bone cancer and other biomedical applications.

1. Introduction

In recent years, assembling nanomaterials into special nanostructures has gained considerable scientific attention because of their extensive range of biomedical applications, such as magnetic resonance imaging, drug-delivery, as well as the thermo-seeds embedded in bioactive materials which are utilized for bone cancer treatment using the hyperthermia method [1–3]. Magnetic nanomaterials have frequently been used for the purpose of hyperthermia treatment and the killing of cancer cells in bones, which involves localized heating of infected parts of the body by applying an alternating magnetic field. But magnetic nanoparticles are prone to aggregation and rapid biodegradation when they are exposed to a biological system [4] which can be problematic considering the importance of biosafety of the nanoparticles in medical applications. The materials that are compatible with bone tissue are preferred for the treatment of bone repair and related cancer therapy. Hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$) is a biologically active material that has drawn great attention from researchers due to its excellent biocompatibility, osteoconductive properties and a chemical structure similar to apatite in the human skeletal system [5–7]. Hydroxyapatite is widely applied as a biomedical material, including such uses as bone fillers, hard and soft tissue repairs, drug and gene delivery systems, protein separation and column chromatography for rapid fractionation of biomolecules [8–12]. In addition, HA materials are also potential candidates for use in cell targeting, near-infrared (NIR) fluorescence labeling, imaging and diagnostic materials [13,14]. Recently, there is growing interest in hydroxyapatite-based nanocomposites with a magnetic property as drug delivery carriers to precisely target the desired organs or tissues inside the body and thus significantly reduce unnecessary damage to healthy tissue by applying local heat through an external magnetic field [15]. Carbon nanotubes (CNTs), especially multi-walled carbon nanotubes (MWCNTs) have been considered as potential candidates for a reinforcing agent of hydroxyapatite due to their unique thermal, electronic, magnetic properties and as innovative carriers for bone morphogenetic protein [16–18]. Moreover, CNT-based biomaterial composites are proven to be suitable for cell growth and growing enzyme activity [19,20]. Functionalized carbon nanotubes (f-CNTs) act as carriers for the delivery of a wide range of therapeutic agents [21]. The healing potential of a defective bone is significantly enhanced when therapeutic agents are delivered through HA nanocarriers [22,23]. Therefore, it is important to develop the HA/f-MWCNTs nanocomposites with an improved magnetic property so that they can be used as a thermal seeds by magnetically induced hyperthermia, killing cancer cells at temperatures > 43 °C for bone cancer treatment. To maximize the effects of MWCNTs for the aforementioned biomedical applications, they have to be functionalized or chemically modified in order to improve their biocompatibility by the presence of

* Corresponding author at: Department of Electrical and Electronic Engineering, International Islamic University Chittagong, Chittagong 4203, Bangladesh.
E-mail address: mjaynul@gmail.com (M.J. Abden).

http://dx.doi.org/10.1016/j.matlet.2016.01.060
0167-577X/

functional groups. An innovative and effective process is introduced to functionalize multi-walled carbon nanotubes (f-MWCNTs) in this paper to achieve debundling as well as in situ fabrication of HA/3 wt% f-MWCNTs nanocomposites, which is expected to develop their ferromagnetic properties, suggesting potential applications in bone tissue treatment and other biomedical applications.

2. Experimental

The carboxylic groups on pristine MWCNTs (purity > 95%, 10–15 nm in diameter, 0.1–10 μm in length) were introduced by refluxing them in a mixture of 3:1 concentrated H_2SO_4 and HNO_3 under stirring at 70 °C for 4 h, left to sit for 12 h, and then stirring for an additional 2 h at the same temperature. The resulting solution was diluted with DI water and left overnight. Afterward, the mixture was vacuum filtered and washed with DI water repeatedly until it had a neutral pH. The resulting carboxylated MWCNTs (f-MWCNTs) were dried in a vacuum at 60 °C for 12 h. The f-MWCNTs were then dispersed in DI water, mixed with a 1 M aqueous solution of $Ca(OH)_2$ and stirred for 1 h under ambient conditions. The stock solution of H_3PO_4 of 0.6 M, used as an initiator was added dropwise under constant stirring at room temperature. The solution was adjusted to 10.5 pH by using NH_4OH. The relative amounts of reactants were calculated to maintain a Ca/P ratio of 1.67. The HA grafted f-MWCNTs thus obtained was centrifuged and dried in a vacuum at 90 °C for 6 h. The sample was ball milled by using a high-energy planetary ball mill (Retsch, PM 100 Japan) at 400 rpm for 3 h in ethanol. To minimize contamination during milling a zirconia pot and balls (10 mm diameter) with a ball-to-powder weight ratio of 10:1 were used. This solution was then dried at 50 °C for 24 h to remove the ethanol. The f-MWCNT content in these samples was 3 wt% by controlling the amount of f-MWCNT and HA matrix. Powder compacts with dimensions of 10 mm × 6 mm were formed by pressing at 150 MPa. The pressureless sintering was performed at 1050 °C by maintaining at a heating rate of 5 °C/min for holding time 2 h in a vacuum atmosphere. The cooling rate was 5 °C/min.

The morphology and dispersion of f-MWCNTs in HA matrix were carried out by using field emission scanning electron microscopy (FESEM; JEOL JSM-7600F, Japan). The crystal phase and chemical bond status of the samples were characterized by a D8 ADVANCE X-ray diffractometer (XRD, Bruker AXS, Karlsruhe, Germany) using Cu-Kα radiation at scan speed of 2° (2θ) per min and a Fourier transform infrared spectrometer (Perkin-Elmer Paragon 500) using KBr powder. Thermogravimetric analysis was carried out using a TG/DTA 6300 (SII NanoTechnology Inc.) under a nitrogen atmosphere between room temperature and 1000 °C at a heating rate of 10 °C/min. The magnetization properties were measured utilizing a vibrating sample magnetometer (VSM) in a magnetic field of ± 10 kOe at room temperature.

3. Results and discussion

Fig. 1 shows the FTIR spectra of the HA/f-MWCNTs composites in the range 400–4000 cm^{-1}. The FTIR spectrum confirmed the bands corresponding to PO_4^{3-} (ν_3-1041, ν_4-607, ν_4-569 cm^{-1}) and CO_3^{2-} (ν_3-1420, ν_2-874 cm^{-1}), respectively. The characteristic peaks at 3414, 3475 and 3550 cm^{-1} are attributed to the OH group. The presence of prominent peaks at 1616 cm^{-1} is assigned to the carboxyl (–COOH) group, indicating that the carboxyl functional group interacted with the hydroxyapatite surface. The FTIR spectrum in the ν_4 PO_4^{3-} domain exhibits the bands at 607 and 569 cm^{-1} which are assigned to PO_4^{3-} ions in apatite sites

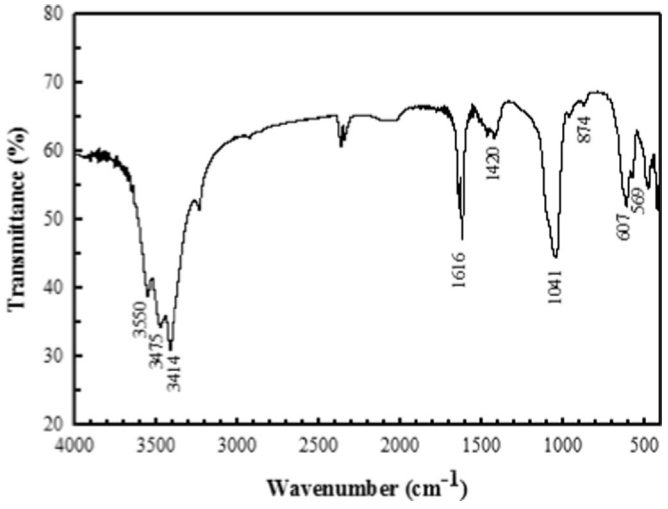

Fig. 1. FTIR spectra of HA/f-MWCNTs composites.

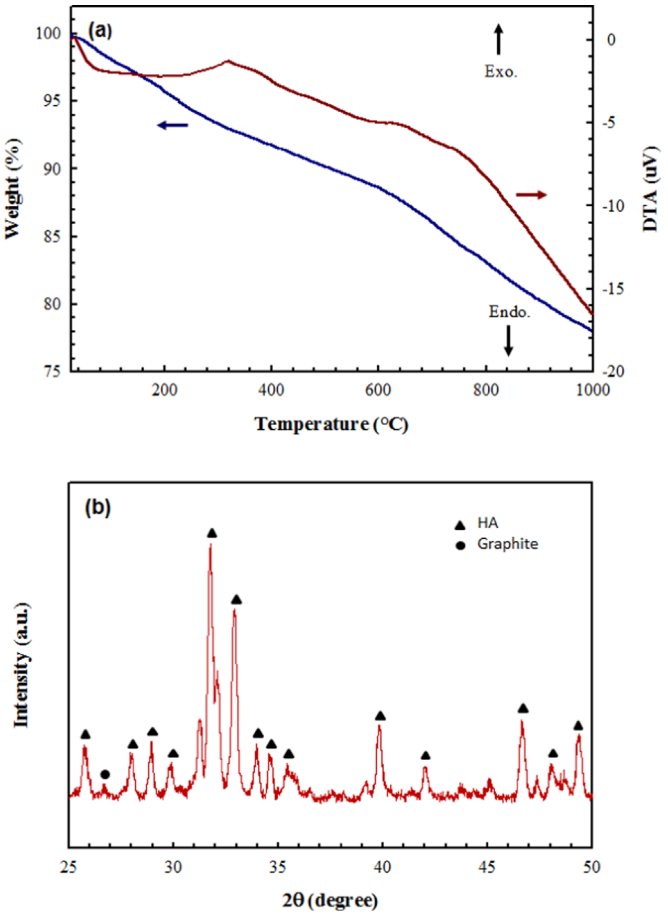

Fig. 2. (a) TG/DTA curves, (b) XRD pattern of HA/f-MWCNTs composites.

[24]. The ν_2 CO_3^{2-} domain exhibits the band at 874 cm^{-1} which may improve the bioactivity of HA and is similar to the characteristic ones observed in bone crystals [24].

Fig. 2(a) shows the TG-DTA curves of HA/f-MWCNTs composites. A gradual and continuous weight loss of 22.02% is detected at total measured temperature ranges. The initial weight loss below 130 °C is due to liberation of absorbed water and the weight loss from 130 to 500 °C may be attributed to the elimination of water released from decarboxylation or condensation of HPO_4^{-2} [25]. The final weight loss is due to the loss of constitution water of HA,