



ELECTRODEPOSITION OF HYDROXYAPATITE/FUNCTIONALIZED CARBON NANOTUBES (HAp/fCNTs) COATINGS ON THE SURFACE OF 316L STAINLESS STEEL

Nguyen Thi Thom^{1,2,*}, Pham Thi Nam¹, Nguyen Thu Phuong¹, Cao Thi Hong¹,
Nguyen Van Trang¹, Nguyen Thi Xuyen¹, Dinh Thi Mai Thanh^{1,2,3}

¹*Institute for Tropical Technology, Vietnam Academy of Science and Technology,
18 Hoang Quoc Viet Street, Cau Giay, Ha Noi*

²*Graduate University of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Ha Noi*

³*University of Science and Technology of Hanoi, Vietnam Academy of Science and Technology,
18 Hoang Quoc Viet Street, Cau Giay, Ha Noi*

*Email: nguyenthomsp@gmail.com

Received: 12 January 2017; Accepted for publication: 11 October 2017

Abstract. The coatings of hydroxyapatite/functionalized carbon nanotubes (HAp/fCNTs) were successfully synthesized on the surface of 316L stainless steel (316L SS) by electrodeposition. To improve the dispersion of CNTs into the electrolyte, CNTs were functionalized in the mixture of 67 % HNO₃ and 98 % H₂SO₄ before electrodeposition coatings to form fCNTs. Different amounts of fCNTs were incorporated into the apatite coatings by adding fCNTs into the electrolyte solution. In this study, Fourier Transform Infrared Spectroscopy (FT-IR), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and mechanical techniques were used to analyze characteristics of HAp/fCNTs coatings. The results show that the HAp/fCNTs nanocomposite coatings contain single phase of HAp and CNTs with the coating thickness of 6.9 μm and the amount of fCNTs in the coatings is 6.95 %. With the presence of fCNTs in HAp coatings, the solubility of the coatings decreases in comparison with pure HAp coatings.

Keywords: 316L SS, electrodeposition, hydroxyapatite, fCNTs, HAp/fCNTs nanocomposite.

1. INTRODUCTION

Research and fabrication of biomedical materials for implants have received considerable interest and intensive research during last few decades as they are used as replacement material for various body parts or organs [1]. Nowadays, the materials often are used for surgery and orthopedics in hospitals such as: 316L stainless steel, cobalt alloy (CoNiCrMo), titanium and the compound of titanium (TiN, TiO₂, Ti6Al4V). These materials are widely used because of the high corrosion resistance ability and good biocompatibility. Despite their successful use but in some case for their long term clinical application, these materials can corrode in the biological environment like human body fluids [2]. To solve this problem, modification the surface of these

materials by the coatings which have biocompatibility as well as improvement of some properties like faster bone healing are new interesting researches.

Hydroxyapatite (HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) as a natural component of bone tissue, is known to be bioactive in living organisms. Synthetic HAp has a similar chemical composition, crystal structure as the natural bone tissue [3, 4]. It has bioactive and high biocompatibility with cells, tissues and can be create direct bonding with immature bone leading to the quick regeneration of bone. Thus, HAp is used as a popular material for bone and tooth implants in the biomaterial field. However, pure HAp coatings have high solubility in physiological environments and poor mechanical properties to be used in any load-bearing applications which is lower compared to human [5]. In order to improve the limitation, fabrication nanocomposite based on HAp and carbon nanotubes (CNTs) are attracting scientists.

Carbon nanotubes (CNTs) have attracted broad attention because of their unique structure and special properties such as: excellent mechanical, high corrosion resistance, unique structural properties, high specific surface area, low density, good biocompatible and small toxicity. Therefore, they are used as reinforcement materials in composite materials based on metals, alloys and polymers with a wide range of applications [5 - 10]. Many studies show that the doped CNTs into components of HAp improves significantly mechanical properties of the materials [5, 11 - 16].

Many methods are used for the development of composite coatings onto the implant surfaces: a Shear Mixing method [17, 18], Sprayed Plasma [19 – 20], Electrophoretic Deposition [11, 21] and Electrodeposition [2, 14]. Among them, electrodeposition is a simple technique to synthesize HAp/CNTs coatings. This method involves low temperature, has good control over the deposition thickness and quality, low energy consumption and also it is an environmental friendly process.

In this study, CNTs were functionalized their surface using the mixture of 67 % HNO_3 and 98 % H_2SO_4 (1:3 volume ratio). And the coatings of HAp/fCNTs nanocomposite were performed successfully on the surface of 316L SS substrate using electrodeposition technique. The effect of fCNTs amount was investigated. It is expected that the presence of fCNTs is able to decrease the solubility, improve the mechanical properties and the bioactivity of the material.

2. EXPERIMENT

2.1. Materials

The substrate is 316L SS sheet (size $100 \times 10 \times 2$ mm, composed of 69.405 % Fe, 17.98 % Cr, 9.34 % Ni, 2.15% Mo, 0.56 % Si, 0.3 % Al, 0.22 % Mn, 0.045 % P. Prior to electrodeposition the surface of 316L SS samples were polished with different grades of SiC emery papers, from P320 to P1200 grind, washed with distilled water, followed by ultrasonic rinsing in distilled water for 10 minutes and then dried at room temperature. Epoxy was used to cover the substrate and limit the working area to 1 cm^2 .

The chemicals used for the experiments were: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ($M = 236.15 \text{ g/mol}$, 99 % pure), $\text{NH}_4\text{H}_2\text{PO}_4$ ($M = 115.03 \text{ g/mol}$, 99 % pure), NaNO_3 ($M = 84.99 \text{ g/mol}$, 99 % pure), 67 % HNO_3 and 98 % H_2SO_4 were from China. Multi-Walled carbon nanotubes (CNTs) with parameters: 90 % pure, diameter from 20 to 100 nm, length 1 - 10 μm was synthesized by chemical vapour deposition (CVD) from Institute of Materials Science, Vietnam.

2.2. Functionalization method of CNTs

Before electrodeposition of nanocomposite coatings, CNTs were chemically functionalized using the mixture of 67 % HNO₃ and 98 % H₂SO₄ acids (1:3 volume ratio). Firstly, 4 g CNTs were solicated in 200 ml mixture of HNO₃ and H₂SO₄ (1:3 volume ratio) at room temperature for 60 minutes. Secondly, the mixture was poured into the round-bottomed flask, heated to 110 °C for 60 minutes using a silicone oil bath and kept refluxing during 60 minutes and cooled to room temperature. The acid solution was filtered using centrifuging and the obtained products were washed with distilled water to pH 7 through paper filter. Finally, obtained functionalized CNTs (fCNTs) were dried in a vacuum oven at 60 °C during 48 h [2]. The results show that CNTs were functionalized successfully through the acid treatment process by the presence of carboxylic acid groups on the surface of CNTs in FT-IR spectra [22].

2.3. Deposition equipment and procedure

The electrolyte solution contained 3×10^{-2} M Ca(NO₃)₂, 1.8×10^{-2} M NH₄H₂PO₄, 0.15 M NaNO₃ with the ratio of Ca/P being 1.67 dissolved in distilled water. The presence of NaNO₃ in the electrolyte solution increases the conductivity of the electrolyte and potentially exploiting the electrochemical reduction of NO₃⁻ ions which contributes to generate OH⁻ [23, 24]. Five different electrolytes with 0, 0.25, 0.5, 0.75 and 1.0 mg/L of fCNTs were prepared, and the nanocomposite coatings were denoted as HAp, HAp/fCNTs-0.25, HAp/fCNTs-0.5, HAp/fCNTs-0.75 and HAp/fCNTs-1.0, respectively. The pH of the electrolyte solution was 4.4.

HAp coatings were synthesized in a cell containing 50 ml of the above electrolyte solutions with three electrodes: the working electrode was a 316L SS sheet; a Pt foil was used as counter electrode (anode) and a Hg/Hg₂Cl₂/KCl (SCE) electrode was used as reference. The deposition temperature was adjusted at 45 °C by a thermostat (VELP, Italia).

The electrodeposition of HAp/fCNTs nanocomposite coatings was carried out on an AUTOLAB (Metrohm, Netherlands) potentiostat-galvanostat under synthesis conditions: scanning potential ranges 0 to -1.65 V/SCE; scanning rates of 5 mV/s with 5 scans at 45 °C. After synthesis process, the obtained coatings were lightly rinsed by distilled water. Then they were dried at the room temperature.

2.4. Characterization of the coatings

The mass of HAp or HAp/fCNTs coatings deposited on the surface of 316L SS substrate was determined by weighing 316L SS samples before and after synthesis by a Precisa analytical balance (XR 205SM-PR, Swiss).

The thickness of coatings was measured by Alpha-Step IQ devices (KLA-Tencor-USA) according to ISO 4288-1998 standards. The thickness value is the average value of 5 measurements.

The adhesion strength between the coatings of HAp or HAp/CNTs and 316L SS substrate was evaluated by tensile testing following an ASTM F1044 standard [25]. Tensile tests were conducted by a computer-controlled universal testing machine (Instron, Model 5500R, US) at a cross head speed of 0.25 centimetre per minute (0.1 inch/minute). The degree of bonding strength was calculated as shown in:

$$\text{Bonding strength (MPa)} = \frac{\text{Maximum load to failure (N)}}{\text{cross - sectional area (m}^2\text{)}} \quad (1)$$

Characteristic groups in the molecular of HAp and HAp/fCNTs were analyzed by Fourier Transform Infrared Spectroscopy. The spectra were recorded by IS10 (NEXUS) using KBr pellet technique at room temperature, in the range from 400 to 4000 cm⁻¹ with 32 scans and 4

cm⁻¹ resolution. The phase components of HAp and HAp/fCNTs were identified by X-Ray Diffraction (XRD) (SIEMENS D5005 Bruker-Germany, Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$)), operated at 40 kV and 30 mA, with step angle of 0.030 °/s and in a 2 θ degree range of 20°-70°. The crystal diameter of HAp in HAp/fCNTs nanocomposite can be calculated from the XRD pattern based on the Scherrer equation:

$$D = \frac{0.9 \lambda}{B \cos\theta} \quad (2)$$

where, D (nm) is crystallite size, $\lambda = 0.15406 \text{ nm}$ is the wavelength of the X-ray radiation (CuK α), θ (rad) is the diffraction angle, and B is the full width at half-maximum FWHM (rad) of the peak at (211) plane.

The surface morphology of HAp/316L SS and HAp/fCNTs/316L SS coatings were characterized using a Hitachi S-4800 Scanning Electron Microscopy (SEM). The content of fCNTs in the HAp/fCNTs coatings was determined by the disintegrate of 1g HAp/fCNTs in 10 % CH₃COOH solution. After that, fCNTs is separated by filter and washed with distilled water, dried at 80 °C for 24 hours. The amount of fCNTs was determined using Precisa XR 205 SM-DR balance.

The dissolution of HAp/316L SS and HAp/fCNTs/316L SS coatings was determined through Ca²⁺ concentrations dissolved from the coatings when they were immersed in 20 ml physiological saline solution (0.9 % NaCl) with different time: 7, 14 and 21 days. Atomic Absorption Spectrometry (AAS) was used to measure Ca²⁺ concentration on iCE 3500.

3. RESULTS AND DISCUSSIONS

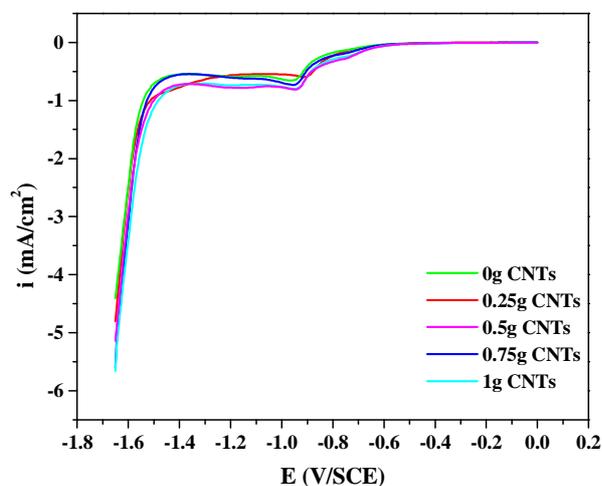


Figure 1. The cathodic polarization curves of 316L SS in the electrolyte solution with the different amounts of fCNTs from 0 to 1 g/L.

The coatings of HAp and HAp/fCNTs nanocomposites were conducted on 316L SS at the condition: the scanning potential range from 0 to -1.65 V/SCE, 5 mV/s, 5 scans at 45 °C in 50 mL of the electrolyte solutions with the different amount of fCNTs: 0, 0.15, 0.5, 0.75 and 1 g/L. Figure 1 presents the cathodic polarization curves of 316L SS in the above electrolyte solutions. Generally, the curves are similar but when the amount of fCNTs in the electrolyte

solution increases from 0 to 1 g/L, the current density as well as charge increases (Table 1). It can be explained as following: the amount of fCNTs increases leading to the conductivity of the electrolyte increases.

The FT-IR spectra of HAp and HAp/fCNTs synthesized with various amounts of fCNTs in the electrolyte solution are presented in Figure 2. The FT-IR spectrum of HAp appears characteristic peaks of hydroxyapatite. Absorption bands at 3440 cm^{-1} and 1640 cm^{-1} are characterised for stretching vibration of -OH. The presence of PO_4^{3-} group is observed at 1040 cm^{-1} ; 560 and 600 cm^{-1} . The FT-IR spectra of HAp/fCNTs nanocomposite present characteristic peaks of HAp and fCNTs. The characteristic band of C-OH in -COOH group of fCNTs at 1385 cm^{-1} move back to 1380 cm^{-1} in the spectrum of HAp/fCNTs nanocomposite. It indicates the molecular interaction between Ca^{2+} in HAp and $-\text{COO}^-$ group of fCNTs in the nanocomposite [2, 26]. Thus, all these bands confirm the formation of HAp/fCNTs nanocomposite coatings on 316L SS.

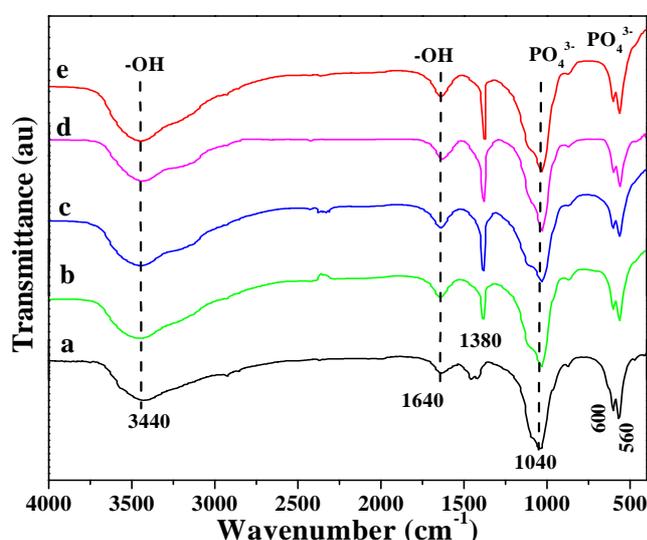


Figure 2. FT-IR of (a) HAp and HAp/fCNTs with the different amounts of fCNTs: (b) 0.25, (c) 0.5, (d) 0.75 and (e) 1 g/L in the electrolyte solution.

Table 1 shows that with the presence of fCNTs in the electrolyte solution, the mass and the thickness of HAp/fCNTs coatings decrease. It can be explained by the special structure of fCNTs. fCNTs are long tubes with voluminous molecular structure which prevents the formation of HAp/CNTs coatings on the surface of 316L SS. However, the presence of fCNTs in the component of nanocomposite improves significantly the adhesion strength between the coatings and the 316L SS substrate. The adhesion strength of pure HAp coatings is 5.35 MPa. With the presence of 0.25 g/L fCNTs in the electrolyte solution, the adhesion strength increases strongly about twice in comparison with pure HAp coatings. The amount of fCNTs increases from 0 to 0.5 g/L, the adhesion strength increases from 5.35 to 13.2 MPa, respectively. If the amount of fCNTs raises more (0.75 g/L and 1.0 g/L), the adhesion strength of the coatings decreases. The results are explained as following: at small amount of fCNTs (0.25 and 0.5 g/L), the obtained coatings are tighter than pure HAp coatings. It is caused by the formation of hydrogen bonding between $-\text{COOH}$ groups in fCNTs and $-\text{OH}$ groups of HAp. However, the bigger amount of fCNTs which aggregate to form a non

uniform dispersion of the nanocomposite [26]. Therefore, the fCNTs amount of 0.5 g/L is chosen in this study. The images of the HAp/316L SS and HAp/fCNTs-0.5/316L SS after the adhesion strength test are showed in Figure 3a and Figure 3b. The next researches, the characteristic properties of HAp and HAp/fCNTs-0.5 coatings will be analyzed.



Figure 3a. The images of HAp/316L SS after the adhesion strength test follows ASTM F 1044 standard.



Figure 3b. The images of HAp/fCNTs-0.5/316L SS after the adhesion strength test follows ASTM F 1044 standard.

Table 1. The variation of charge, mass, thickness and adhesion strength of HAp/316L SS and HAp/fCNTs/316L SS synthesized with different amounts of fCNTs.

fCNTs (g/L)	The charge Q (C)	The mass (mg/cm ²)	The thickness (μm) ISO 4288-1998	The adhesion strength (MPa)
0	1.81	2.63	8.66	5.35
0.25	1.92	2.13	6.92	10.24
0.50	2.05	2.10	6.9	13.20
0.75	2.15	1.96	6.70	11.19
1.00	2.31	1.74	5.70	9.35

The XRD patterns of HAp and HAp/fCNTs-0.5 nanocomposite synthesized with the presence of 0.5 g/L fCNTs are shown in Figure 4. Both of the samples present the characteristic diffraction peaks of HAp which are observed at 2θ values of 25.93° and 31.81° corresponding to (002), (211) planes. With HAp/fCNTs nanocomposite, a high intensity diffraction peak assigned to a graphite crystallographic (002) plane of CNTs is observed at 26.05° . All these peaks confirm the presence of HAp and CNTs in the component of the nanocomposite. From the Xray diffraction patterns, the diameter of HAp in HAp/fCNTs nanocomposite following the Scherrer (Eq.2) is 5.7 nm.

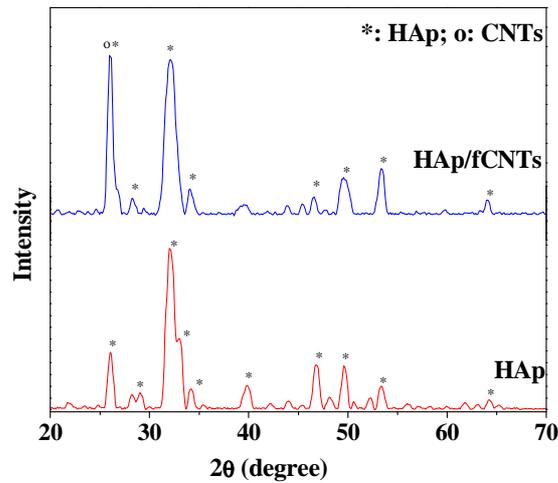


Figure 4. XRD patterns of HAp and HAp/fCNTs.

Table 2 shows amount of fCNTs in the deposited HAp/fCNTs coatings which is determined by the disintergrate of HAp/fCNTs coatings in 10% CH₃COOH solution. The amount of fCNTs achieves about 69.51 mg in 1000 mg HAp/fCNTs coatings corresponding 6.95%. This result is the average value of 3 measurements.

Table 2. The content of fCNTs in HAp/fCNTs coatings was determined using the dissolution of the coatings.

Times	1	2	3	Average
Amount of fCNTs (mg)	69,60	70,05	68,89	69,51 ± 0,33

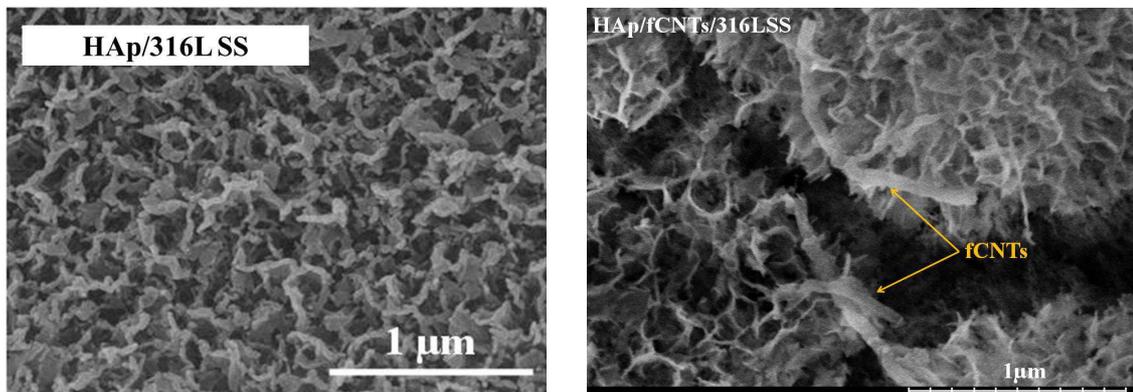


Figure 5. SEM images of HAp/316L SS and HAp/fCNTs-0.5/316L SS coatings.

SEM images of HAp/316L SS and HAp/fCNTs-0.5/316L SS coatings are presented in Figure 5. Both coatings are similar with coral-like shape. With the presence of 0.5 g/L fCNTs in the electrolyte solution, we can see the formation of HAp crystals which cling on the surface of fCNTs.

In this section, HAp/316L SS and HAp/fCNTs-0.5/316L SS coatings were synthesized in the electrolyte solution containing 3×10^{-2} M $\text{Ca}(\text{NO}_3)_2$, 1.8×10^{-2} M $\text{NH}_4\text{H}_2\text{PO}_4$, 0.15 M NaNO_3 with and without 0.5 g/L fCNTs in the scanning potential range from 0 to -1.65 V/SCE, scanning rate of 5 mV/s, 5 scans at 45 °C. After that, the dissolution of these materials were determined by the concentration of Ca^{2+} dissolved from the coatings when they were immersed into 20 ml of physiological saline solution 0.9 % NaCl at 37 °C.

Table 3 presents the concentration of Ca^{2+} dissolved from HAp/316L SS and HAp/fCNTs/316L SS in 0.9 % NaCl solution, it shows that the dissolution of the coatings increases according to immersion time for both coatings. During immersion time, the dissolution of HAp/316L SS is always bigger than that of HAp/fCNTs/316L SS coatings. The results confirm that the presence of fCNTs in the coating component reduces significantly the dissolution of nanocomposite. That is explained: The -COOH groups on the surface of fCNTs creates hydrogen-bonds with -OH groups of HAp, so CNTs act as bridge linkings with HAp crystals and lead to the formation of the tighter coatings in comparison to the pure HAp coatings [27].

Table 3. The concentration of Ca^{2+} in the solution after immersing HAp/316L SS and HAp/fCNTs-0.5/316L SS into 0.9 % NaCl solution.

Immersion time (days)	Ca^{2+} (mg/L)	
	HAp/316L SS	HAp/fCNTs/316L SS
7	20.6	13.1
14	25.3	16.6
21	30	19.5

4. CONCLUSIONS

Hydroxyapatite/functionalized carbon nanotubes (HAp/fCNTs) coatings were synthesized successfully on the surface of 316L SS substrate by electrodeposition technique. The presence of fCNTs in the HAp/fCNTs nanocomposite decrease the solubility and improve the mechanical properties of the material. In our next studies, we will continue to investigate the effect of some factors to the coating properties and test the biocompatibility and the corrosion behavior of the HAp/fCNTs nanocomposite in simulated body fluid solution.

Acknowledgments. This work was supported by Vietnam Academy of Science and Technology and Graduate University of Science and Technology.

REFERENCES

1. Ciobanu G., Carja G., and Ciobanu O. - Structural characterization of hydroxyapatite layer coatings on titanium supports, *Surf. Coat. Technol* **202** (2008) 2467–2470.
2. Gopi, D., Shinyjoy E., Sekar M., Surendiran M., Kavitha L., and Sampath Kumar T.S. - Development of carbon nanotubes reinforced hydroxyapatite composite coatings on titanium by electrodeposition method, *Corrosion Science* **73** (2013) 321–330.
3. Albayrak O., El-Atwani O., and Altintas S. - Hydroxyapatite coating on titanium substrate by electrophoretic deposition method: Effects of titanium dioxide inner layer on adhesion strength and hydroxyapatite decomposition, *Surface and Coatings Technology* **202** (2008) 2482–2487.

4. Morks M.F., and Kobayashi A. - Effect of gun current on the microstructure and crystallinity of plasma sprayed hydroxyapatite coatings, *Applied Surface Science* **253** (2007) 7136–7142.
5. Ashley A. W., Serena M. B., and Lan A. K. - Hydroxyapatite–carbon nanotube composites for biomedical applications: A review, *Int. J. Appl. Ceram. Technol.* **4** (2007) 1–13.
6. Ajayan P.M., - Nanotubes from carbon, *Chem. Rev.* **99** (1999) 1787–1799.
7. Cholpek J., Czajkowska B., Szaraniec B., and Beguin F., - In vitro studies of carbon nanotubes biocompatibility, *Carbon* **44** (2006) 1106–1111.
8. Price R.L., Waid M.C., Haberstroh K.M., and Webster T.J. - Selective bone cell adhesion on formulations containing carbon nanofibers, *Biomaterials* **24** (2003) 1877–1887.
9. Peigney A. - Composite materials: tougher ceramics with nanotubes, *Nat. Mater.* **2** (2003) 15–16.
10. Susmita M., Biswanath K., Abhijit C., and Swarnendu S.. - Effect of functionalisation of CNT in the preparation of HAp–CNT biocomposites, *Ceramics International* **41** (2015) 3766–3774.
11. Cengiz K. - Electrophoretic deposition of carbon nanotube-reinforced hydroxyapatite bioactive layers on Ti–6Al–4V alloys for biomedical applications, *Ceramics International* **34** (2008) 1843–1847.
12. Rajesh R., Senthilkumar N., Hariharasubramanian A., Dominic Ravichandran Y. - Review on hydroxyapatite-carbon nanotube composites and some of their applications, *International Journal of Pharmacy and Pharmaceutical Sciences* **4** (2012) 23-27.
13. Debrupa L., Sanat G., and Arvind A. - Carbon nanotube reinforced hydroxyapatite composite for orthopedic application: A review, *Materials Science and Engineering C* **32** (2012) 1727–1758.
14. Xibo P., Yongxiang Z., Rui H., Zhongjie L., Lingyang T., Jian W., Qianbing W., Xiaoyu L., and Hong B. - Single-walled carbon nanotubes/hydroxyapatite coatings on titanium obtained by electrochemical deposition, *Applied Surface Science* **295** (2014) 71-80.
15. Xu J.L., Khor K.A., Sui J.J., and Chen W.N. - Preparation and characterization of a novel hydroxyapatite/carbon nanotubes composite and its interaction with osteoblast-like cells, *Materials Science and Engineering C* **29** (2009) 44–49.
16. Debrupa L., Virendra S., Anup K. K., Sudipta S., and Arvind A. - Carbon nanotube toughened hydroxyapatite by spark plasma sintering: Microstructural evolution and multiscale tribological properties, *Carbon* **48** (2010) 3103–3120.
17. Susmita M., Swarnendu S., and Abhijit C. - Mechanical and In vitro Performance of CNT Reinforced Hydroxyapatite Prepared by a Shear Mixing Method, *J Nanomed Nanotechnol.*, volume **4** (3) (2013) doi:10.4172/2157-7439.1000169.
18. Susmita M., Biswanath K., Swarnendu S., and Abhijit C. - Improved properties of hydroxyapatite–carbon nanotube biocomposite: Mechanical, in vitro bioactivity and biological studies, *Ceramics International* **40** (2014) 5635–5643.
19. Kantesh B., Rebecca A., Tapas L., Melanie A., Jorge T., Eric C., and Arvind A. - Plasma-sprayed carbon nanotube reinforced hydroxyapatite coatings and their interaction with human osteoblasts in vitro, *Biomaterials* **28** (2007) 618–624.

20. Kantesh B., Yao C., Sandip P. H., Narendra B. D., and Arvind A. - Tribological behavior of plasma-sprayed carbon nanotube-reinforced hydroxyapatite coating in physiological solution, *Acta Biomaterialia* **3** (2007) 944–951.
21. Długon E., Niemiec W., Frazek-Szczypta A., Jelen P., Sitarz M., and Błazewicz M. - Spectroscopic studies of electrophoretically deposited hybrid HAp/CNT coatings on titanium, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **133** (2014) 872–875.
22. Vinayan B.P., Rupali N., Raman V., Rajalakshmi N., Dhathathreyan K.S., and Ramaprabhu S. -Synthesis of graphene-multiwalled carbon nanotubes hybrid nanostructure by strengthened electrostatic interaction and its lithium ion battery application, *J. Mater. Chem* **22** (2012) 9949-9956.
23. Lin D.Y., and Wang X.X. - Electrodeposition of hydroxyapatite coating on CoNiCrMo substrate in dilute solution, *Surface & Coatings Technology* **204** (2010) 3205–3213.
24. Myriam N., Olivier D., Oscar R.M., and Bernard T. - The nitrate reduction process: A way for increasing interfacial pH, *Journal of Electroanalytical Chemistry* **600** (1) (2007) 87–94.
25. ASTM International, “Standard test method for shear testing of calcium phosphate coatings and metallic coatings,” ASTM F1044, ASTM International, WestConshohocken, Pa, USA, 2005, <http://www.astm.org>.
26. Sánchez P E., and Reyes G. J. - Determination of the Point and Space Groups for Hydroxyapatite by Computer Simulation of CBED Electron Diffraction Patterns, *Revista Mexicana de Física* **51** (2005) 525-529.
27. Réka B., Gabriel K., Erzsébet S. B., Mircea V. D., Adrienn S., Balázs Z., József K., Ladislau K. N., and Melinda C. - Preparation and characterization of carboxyl functionalized multiwall carbon nanotubes–hydroxyapatite composites, *Ceramics International* **41** (2015) 12717–12727.