



A novel and rapid route to synthesize polyvinyl alcohol/calcium phosphate nanocomposite coatings by microwave assisted deposition



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ABSTRACT

The nanocomposite of polyvinyl alcohol (PVA) and hydroxyapatite (HAp) was deposited on titanium by an innovative microwave assisted deposition. The deposition parameters, such as polymer concentration and deposition time, were optimized to attain a homogeneous, crack free and adhesive coating on the substrate. The nanocomposite coatings were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM); in addition, photoluminescence and wettability were also examined. There was no significant variation in the crystallite size and microstrain; however, enhanced photoluminescence and reduced particle size, pore size and wettability were observed on increasing the PVA incorporation. This technique is fast and versatile, and could produce a homogeneous nanocomposite coating simultaneously, on many substrates in a single step. The properties of nanocomposite coatings enable them to be used as promising materials for bone replacement, protein adsorption and biosensors.

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1. Introduction

Metals such as titanium and its alloys have been used as implants in dental and orthopedic applications. However, when they interact with the body fluid, toxic metal ions were released which could damage the nearby tissues. Metals possess deprived bioactive and weak adhesion strength with the surrounding bone tissues [1]. Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAp) was coated on a metal surface to enhance the bone growth at the interface of the prosthetic devices. HAp is one of the calcium phosphate phases, and its chemical composition and structure closely resemble those of natural bone and teeth. However, HAp is not biodegradable, and is not suitable for load bearing applications. Polyvinyl alcohol (PVA) is biodegradable and biocompatible to living organs and cells, and could therefore be made into a composite with HAp to overcome these drawbacks [2].

The various techniques for depositing calcium phosphate onto the metallic implants are biomimetic [3], electrochemical [4], pulse laser [5], radio frequency-magnetron sputtering [6], sol-gel [7] and microwave assisted chemical bath deposition [8]. However, most of these techniques are complicated, time-consuming and expensive. In most cases, the bonding between the HAp coating and the metallic substrate is weak, and difficult to obtain in a short time [9–11].

Here, we report for the first time the synthesis of homogeneous PVA–HAp nanocomposite coatings by microwave irradiation, which is rapid and cost-effective.

2. Materials and method

The nanocrystalline HAp was synthesized using calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Merck), diammonium hydrogen phosphate ($(\text{NH}_4)_2 \cdot \text{HPO}_4$, Merck) and ammonia solution (Merck). 0.6 M $(\text{NH}_4)_2 \cdot \text{HPO}_4$ was dissolved in deionized water. 1.0 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was added drop by drop to the $(\text{NH}_4)_2 \cdot \text{HPO}_4$ solution with continuous stirring at a constant pH 10. The precipitated solution was subjected to microwave irradiation (house-hold microwave oven 900 W and 2.45 GHz) for a period of 30 min. The precipitate was washed and dried in a hot air oven at 80 °C.

0.5 g of the synthesized HAp was added to various concentrations of PVA, say 0.0%, 0.5%, 1% and 1.5%, ascribed as OPHAp, 0.5PHAp, 1PHAp and 1.5PHAp respectively, dissolved in deionized water, and heated at 60 °C. Titanium (1 cm × 1 cm × 1 mm) was used as the substrate, and was immersed in the PVA/HAp solution and irradiated, using a microwave for 2 min and dried at 60 °C.

The samples were analyzed using Bruker XRD $\text{CuK}\alpha$ radiation (0.154 nm) with a step size 0.02° in the 2θ range from 10° to 75°, in a continuous scan mode. The crystallite properties were calculated using MAUD (Material Analysis Using Diffraction). BOMEM DA-8

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FTIR (KBr pellet technique) was used to investigate the vibrational modes of the sample. The surface morphology was examined using SEM (Carl Zeiss MA15/EVO 18). The photoluminescence spectra were obtained, using the Horiba Jobin Yvoun monochromator. The wettability of the samples was evaluated through water contact angle measurements.

3. Results and discussion

The XRD patterns of the nanocomposite coatings of PVA/HAp were in good agreement with the standard JCPDS value of HAp (09-0432) (Fig. 1A). The intensity of the peaks at 11.4° and 19.6° , corresponding to the crystalline phase of PVA, was enhanced (1.5PHAp). There was no significant variation in the average crystallite size and microstrain of the nanocomposite coatings, whereas the lattice parameters were enhanced due to the lattice expansion with an increase in the PVA incorporation Table 1 [12].

The FTIR analysis of the nanocomposite coatings is shown in Fig. 1B. The absorption bands at 3577 and 3448 cm^{-1} correspond to the hydroxyl stretching mode of HAp. The band at 3577 cm^{-1} was absent at higher concentrations of PVA (1.5PHAp) due to the intermolecular hydrogen bonding between HAp and PVA. The peaks at 634 cm^{-1} and at 1640 cm^{-1} were assigned to the vibrational and bending modes of the hydroxyl group of HAp. The out of plane vibration of O–H and C–H of PVA was revealed at 831 cm^{-1} (Fig. 1B(b)–(d)). The peak at 1735 cm^{-1} was due to the stretching of C=O from the acetate group of PVA. The PVA stretching band of the C–H group was noticed at 2928 cm^{-1} (Fig. 1B(b)–(d)). The weak band at 1455 cm^{-1} corresponding to the stretching mode of CO_3^{2-} is attributed to the adsorbed CO_2 from the atmosphere during preparation. The peak present at 1382 cm^{-1} could be due to the N–O stretch of NO_3^- . The absorption peaks at 1091 and 1031 cm^{-1} correspond to the asymmetric stretching (ν_3) of the phosphate group of HAp. The peaks at 565 and 604 cm^{-1} were attributed to the bending mode (ν_4), and the band that appeared at 962 cm^{-1} to the symmetric stretching mode of the phosphate group [13–15].

The thicknesses of 0PHAp, 0.5PHAp, 1PHAp and 1.5PHAp were $56 \pm 1\ \mu\text{m}$, $310 \pm 1\ \mu\text{m}$, $322 \pm 1\ \mu\text{m}$ and $120 \pm 1\ \mu\text{m}$ respectively (Fig. 2a–d). On increasing the PVA concentration, the thickness of the nanocomposite coatings increased, whereas at a higher concentration (1.5PHAp), it was reduced. The surface of the coatings had spherical particles with pores (Fig. 2e–h). The

particle sizes of 0PHAp, 0.5PHAp, 1PHAp and 1.5PHAp were $4 \pm 0.5\ \mu\text{m}$, $1 \pm 0.1\ \mu\text{m}$, $0.5 \pm 0.1\ \mu\text{m}$ and $0.4 \pm 0.1\ \mu\text{m}$ respectively, with respective pore sizes of $3 \pm 0.2\ \mu\text{m}$, $0.8 \pm 0.2\ \mu\text{m}$, $0.6 \pm 0.1\ \mu\text{m}$ and $0.5 \pm 0.1\ \mu\text{m}$. The particle and pore sizes of the nanocomposite coatings were reduced, due to an increase in the PVA incorporation, which leads to a decrease in the agglomeration of particles.

The photoluminescence (PL) spectra of the nanocomposite coatings excited at a wavelength of 244 nm are shown in Fig. 3A. With an increase in PVA incorporation, there will be an enhanced intermolecular hydrogen bonding of PVA and HAp as confirmed by the broadening of the peak at 3577 cm^{-1} (Fig. 1B(d)), leading to an increase in the electrons and holes in the nanocomposite coating. When the coating was excited by the photons, the PL emission intensity was enhanced due to the increase in the radiative recombination of the electrons and holes pairs [16,17]. However, there was no significant variation in the band gap energy of the coatings. The PL intensity of the samples could be qualitatively sensed *in-situ* to monitor newly developed bone [18].

The contact angles of 0PHAp, 0.5PHAp, 1PHAp and 1.5PHAp were $79 \pm 0.3^\circ$, $45 \pm 0.3^\circ$, $51 \pm 0.3^\circ$ and $90 \pm 0.3^\circ$ respectively (Fig. 3B). At a lower PVA incorporation ($< 1\%$), the wettability was enhanced whereas it was lowered at the PVA ($> 1.5\%$). The enhancement of the contact angle may be due to the change in the polar component of the surface energy, whereas the decrease in the surface roughness could be due to the decrease in the particle size, leading to an increase in the surface charge of the nanocomposite coating. Therefore, the nanocomposite coatings could assist the adsorption of protein (Bovine Serum

Table 1

Average crystallite size, lattice parameters and microstrain of 0PHAp, 0.5PHAp, 1PHAp and 1.5PHAp.

Sample codes	Average crystallite size ($\pm 0.3\text{ nm}$)	Lattice parameters (\AA)		Microstrain (± 0.0001)
		a = b ($\pm 0.002\ \text{\AA}$)	c ($\pm 0.002\ \text{\AA}$)	
0PHAp	51	9.428	6.881	0.0009
0.5PHAp	53	9.438	6.886	0.0008
1PHAp	52	9.437	6.889	0.0011
1.5PHAp	50	9.454	6.902	0.0016

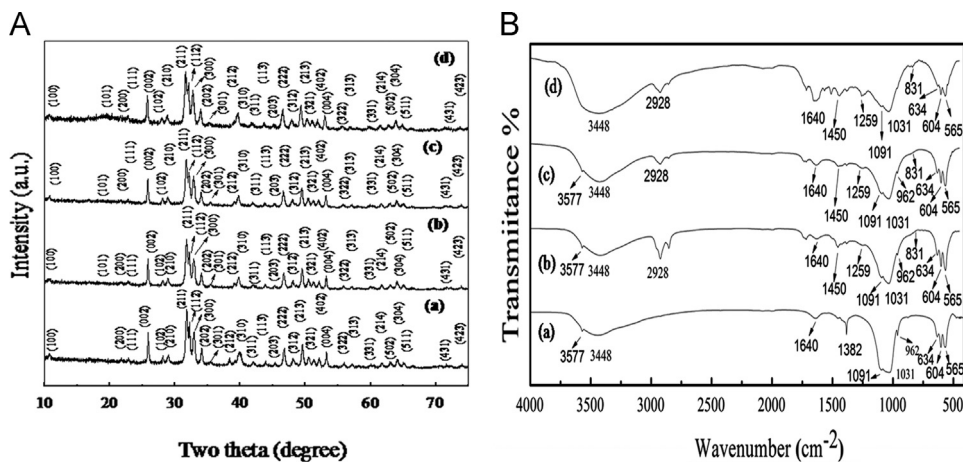


Fig. 1. (A) XRD patterns of (a) 0PHAp, (b) 0.5PHAp, (c) 1PHAp and (d) 1.5PHAp. (B) FTIR spectra of (a) 0PHAp, (b) 0.5PHAp, (c) 1PHAp and (d) 1.5PHAp.

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