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Carbon nanofibers produced from modified electrospun PAN/hydroxyapatite precursors as scaffolds for bone tissue engineering

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ABSTRACT

In the current study we have proposed a method to obtain a carbon/HAp bioactive nanofibrous scaffold. The modified carbon nanofibrous nonwoven' fabrics were obtained by the use of electrospinning and subsequent stabilization and carbonization processes. The modified with HAp powder nanofibrous PAN nonwovens were thermally stabilized using a multi-stage process in the temperature ranging from 100 °C to 300 °C in an oxidative environment and then carbonized at 1000 °C in argon atmosphere. The changes of properties of composite precursor membranes taking place during stabilization and carbonization processes were investigated using the methods of: DSC, TGA, FTIR, SEM, EDX, WAXD and mechanical tests. Bioactivity was determined by assessing the formation of crystalline apatite on the surface of membranes upon immersion in Simulated Body Fluid (SBF). The FTIR, SEM and WAXD investigation clearly prove that hydroxyapatite added to the electrospinning solution was present also in composites nanofibrous nonwovens after stabilization and carbonization process. It was found that due to HAp addition: the significant decrease of fibers average diameter occurs and that the average pore size for modified membranes is smaller than for the unmodified one. On the other hand it was shown that the ceramic additive protects fibers from mass reduction during the stabilization treatment. Finally a drastic increase of mineralization activity of nCF/HAp scaffolds as compared to their nCF counterparts has been proved.

1. Introduction

Recently, a three-dimensional nanofibrous artificial extracellular matrix with high porosity and high spatial interconnectivity prepared by electrospinning has been increasingly applied for bone tissue engineering [1–4]. Nonwoven fibrous membranes comprised of nanofibers have a very high fraction of surface available to interact with cells, which make them ideal for cell attachment. The structure of nonwoven mats prepared by electrospinning is similar to that of natural collagen fibers [5,6] and the nanofibrous artificial ECM can promote cell proliferation, migration and differentiation [7]. Ideal scaffold for bone tissue engineering should mimic natural extracellular matrix (ECM), provide structural support to the repair region and stimulate bone formation.

Carbon fibers have long been considered for hard (i.e., orthopedic and dental) and for soft (i.e., cartilage, tendon, ligament, vascular, etc.) tissue implant due to exceptional mechanical, electrical, thermal, optical and structural properties [8,9]. Carbon fibers have also been shown to be compatible with physiological cells and tissues and nano-dimensioned fibers have excellent conductivity and high strength to weight ratios [10–13]. However, poor biological activity restricts extensive use of carbon fibers in medical applications and therefore it needs to be enhanced [14,15]. Usually hydroxyapatite coatings (HAp, $Ca_{10}(PO_4)_6(OH)_2$,) have been used to promote rapid fixation and bone integration of carbon orthopedic and dental implants. HAp is not only bioactive but also osteoconductive, non-toxic, non-immunogenic, and its structure is crystallographically similar to that of bone [16]. In the past decades, several methods has been reported to deposit calcium phosphate (e.g. HAp) onto implant surfaces, including plasma spray, RF sputtering, pulsed laser deposition, sol–gel, electrophoretic methods, electrochemical deposition [17–21]. However, it is recognized that the mechanical stability of the interface between HAp coating and carbon substrate is a problem either during the surgery or after implantation. Besides it is an additional process, which make the implant production much longer and more expensive. It is well known from earlier research works [22–24] that an addition of hydroxyapatite into carbon microfibers results in an increase of bioactivity of the materials but in order to provide an optimal environment for cells adhesion, proliferation and differentiation, nanofibrous scaffold are more suitable.

Electrospinning method offers advanced opportunities to incorporate nanofillers such as HAp into the nano scale electrospun matrix, which allows to avoid the post-treatment operations (by coating or covering with films) [25–27]. Generally such composite materials are obtained by melt blending or dispersion of the bioactive agent

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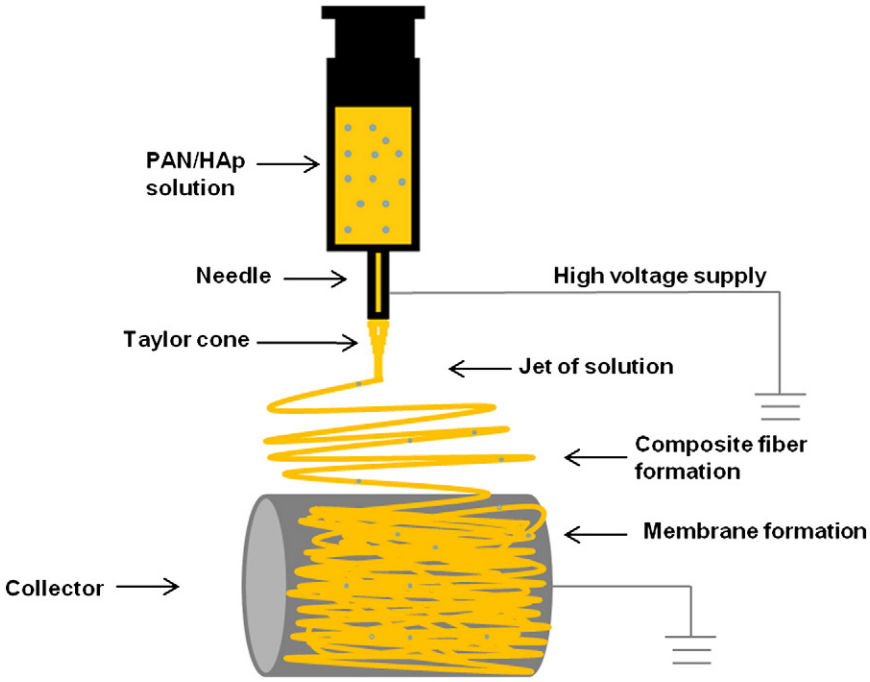

Fig. 1. Schematic diagram of set up of electrospinning apparatus.

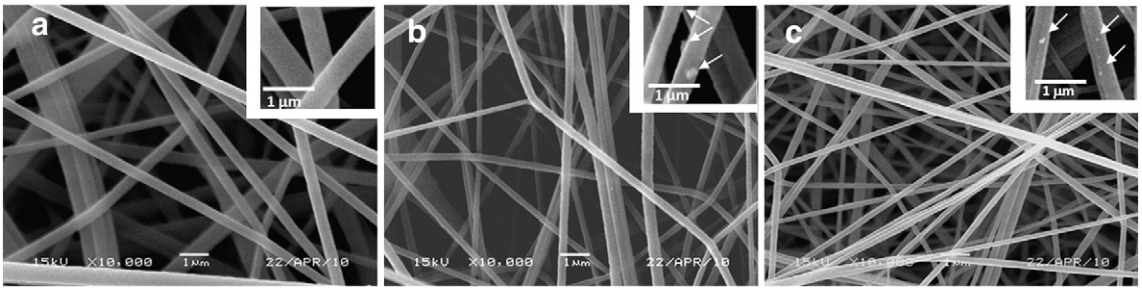

Fig. 2. Microstructure of precursor nanofibrous membranes (a) nPAN, (b) nPAN/3%HAp, (c) nPAN/5%HAp.

in the polymer solution. Electrospun composite nanofibers allow a unique blend of properties, such as bioactivity of inorganic materials (calcium phosphates), and excellent flexibility and moldability of polymers (e.g. polyacrylonitrile — precursor of carbon fibers), while they still can maintain other functional properties of either constituent [28]. Therefore incorporation of hydroxyapatite into a nanofibrous carbon matrix allows not only to mimic the natural fibrous structure of the bone but also to enhance the biological response of the scaffold.

The aim of the work was to obtain bioactive character of carbon nanofibrous nonwoven without an additional coating process with HAp. The research efforts have focused on fabrication of HAp containing carbon nanofibers to produce three-dimensional, porous, bioactive, carbon nonwovens, which could serve as scaffolds for the treatment of bone tissue defects. For this goal electrospun nonwovens composed of PAN and PAN/HAp nanofibers (with HAp content of 3 wt.% and 5 wt.%) have been fabricated and broadly characterized before and

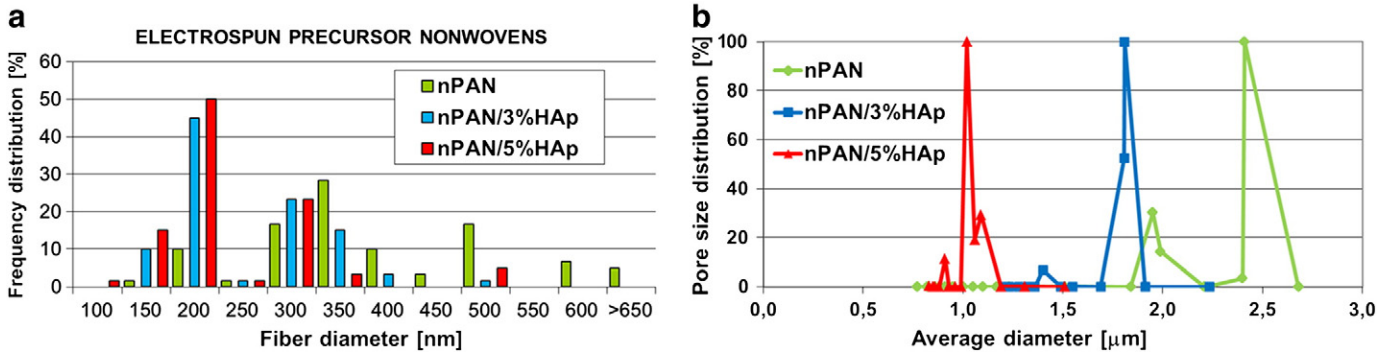

Fig. 3. (a) Fibres diameter distribution; (b) Pore size distribution in precursor membranes.