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Development of nano-hydroxyapatite coating by electrohydrodynamic atomization spraying

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Abstract Electrohydrodynamic atomisation (EHDA) spraying of a hydroxyapatite (HA) suspension consisting of nano-particles (nHA) has been used to produce a HA coating comprising of nanostructured surface topography. In EHDA the suspension is jetted from a needle under an electric field. Obtaining the stable cone-jet mode of EHDA is critical to improve the quality and optimise the morphology of HA coatings, therefore a systematic investigation of the effects of several key processing parameters, such as suspension flow rate, applied voltage and distance between the needle and substrate, and needle size was carried out in this work. The HA coatings processed under different spraying parameters were compared and then scored according to uniformity and microstructural integrity. It was found that all of these parameters had a very significant influence on the morphology of nHA coating prepared. Under an optimised processing condition, where a needle orifice diameter of 300 μm, kept at a distance of 20 mm from the substrate, a flow rate of 20 μL/min, and the applied voltage kept within 4.3 kV and 5.2 kV, a uniform nHA coating was obtained. This is a crucial step forward in obtaining advanced nano-hydroxyapatite coatings of high quality for biomedical applications by using EHDA spraying.

1 Introduction

Metallic implant materials, e.g. titanium and its alloys, have been widely used in load-bearing hip prostheses and dental implants due to their excellent mechanical properties, and corrosion resistance in biological environments. To overcome the problem of lacking direct bone bonding to the metallic implants, the most successful approach so far is to apply a bioactive coating on their surface.

Hydroxyapatite (HA) is well known to promote direct bone apposition [1, 2], and nanometre scale HA forms the inorganic constituent of human bone [3]. Therefore, nHA is widely chosen as the bioactive coating material for incorporation with metallic implants. In the past two decades, HA coated metallic implants have been used very successfully in dental and orthopaedic applications [4–6]. At present, there are various approaches of incorporating HA or other bioceramics to the surface of metallic implants, e.g. plasma spraying, biomimetics, sputtering and electrophoretic depostion [7–10]. Plasma spraying is the most widely used for producing HA coated metallic implants. However, these methods either involve high temperature, or are non-cost effective or technically cumbersome.

Electrohydrodynamic atomisation (EHDA) spraying is a simple, economical and room temperature process, capable of producing a uniform coating [11, 12]. It also offers the advantages of easy control of a large coverage area and compatibility with micro-fabrication technology. Thus, recently, more and more attention is being paid on the study and investigation of this novel processing technique.

Basically, this process consists of a grounded electrode and a needle (nozzle), which is connected to a high voltage supply. The HA suspension is fed to the needle by a pump at a controlled flow rate. The flowing medium is subjected to an electrical field, which is generated by the applied voltage between the nozzle and ground electrode, and generates an elongated jet, which subsequently detaches from the body of suspension and disintegrates into droplets [13]. The jet and droplet generation are classified into

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different modes of spraying governed by the geometry of jetting [14]. Out of several different modes, the cone-jet mode, which is the steadiest mode of spraying, regularizes the break-up of the jet to generate fine and uniform droplets of a few micrometers in size [15].

Within cone-jet spraying mode, there are three phenomena. The first is the acceleration of the suspension in the cone. This acceleration process and the shape of the cone are a result of the balance of many parameters, e.g. liquid pressure, liquid surface tension, viscosity and electric stresses. The second phenomenon is the generation of a jet and the break-up of the jet into droplets. The third phenomenon is the evolution of the spray after droplet production. Electrical interaction between highly charged droplets occurs and droplet fission can change the generated droplet size distribution [16–18].

The background to this study can be explained as follows. Suspension flow rate directly affects the velocity of the liquid, and therefore affects the stability of the cone shape and jet break-up process, and thus bears a significant influence on the coating morphology. The applied voltage is critical to the cone formation, the velocity and acceleration of the suspension, and thus affects the jet break-up process. Furthermore, it also has a considerable effect on the highly charged droplet generation process. Therefore, the applied voltage has a considerable influence on the suspension droplet size distribution. The change of the distance between the needle and substrate will change the droplets travel time, which affects the droplet size due to the degree of evaporation of the liquid phase. The droplet size can be very significant in determining the morphology of the final coating. The needle size and the properties of the suspension significantly influence the suspension velocity, affect cone formation and jet break-up processes. Thus, these are also critical to the stability of the cone-jet EHDA mode. Therefore, the control of these parameters is essential for the EHDA process of preparing nHA coated implant materials.

In this study, the influences of several key process parameters on EHDA spraying of nHA suspension, namely needle size, the distance between the needle and grounded substrate, the flow rate and applied voltage were systematically investigated in order to optimise the HA coating on metallic implants.

2 Experimental procedure

2.1 Preparation and characterisation of nHA suspension

nHA was synthesized by a precipitation reaction between calcium hydroxide and orthophosphoric acid. Both reagents were AnalaR grade. 0.3 M orthophosphoric acid was added drop wise to a 0.5 M calcium hydroxide solution under continuous stirring at room temperature while the pH was kept above 10.5 by the addition of ammonia solution. Stirring was maintained for a further 16 h after complete addition of the reactants. The precipitate obtained was aged for a further week and then washed with boiling water.

To make the nHA suspension suitable for EHDA, ethanol was added as a liquid carrier. A range of nHA concentrations (3–12.5 wt.%) was investigated to achieve electrohydrodynamic spray deposition in the stable cone-jet mode. The density, pH, surface tension, viscosity, electrical conductivity and relative permittivity of nHA suspension were measured. All the measuring equipments were initially calibrated using ethanol to validate reference data. The densities of the samples were calculated using the standard density bottle and the pH was measured using a standard pH probe and meter. Surface tension was measured using a Kruss Tensiometer K9 (Du Novy's ring method). Viscosity was evaluated using a Visco-Easy rotational viscometer. Electrical conductivity was assessed using a HACH SensION™ 156 probe. Relative permittivity was estimated using the standard capacitance method. All measurements were performed at the ambient temperature.

2.2 EHDA spraying process

The experimental setup is shown in Fig. 1. The needle was connected to the power supply. The needle was also connected to a syringe, which is fixed on a syringe pump, to control the flow rate. The processing was performed at the ambient temperature, and the spraying time was kept at 60 s unless stated otherwise.

To investigate the influence of needle size on the stability of the cone-jet mode EHDA spraying of nHA suspension, three different needle sizes with in internal diameter of 300 μm, 500 μm and 800 μm were used. In these experiments, the needle to substrate distance was kept at 20 mm. nHA suspension (3 wt.%) was syringed to the

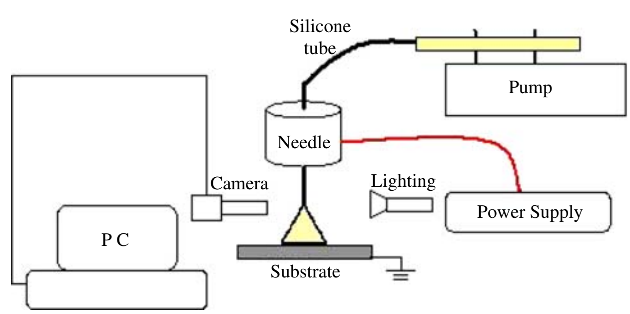

Fig. 1 Schematic diagram illustrating nano-hydroxyapatite coating by an electrohydrodynamic route

Table 1 Properties of ethanol and nHA suspension (6 wt.%), ethanol is the liquid phase of the suspension

Sample	Density/ kgm^{-3}	Viscosity/ mPa s	Surface tension/mNm^{-1}	DC electrical conductivity/Sm^{-1}	Relative permittivity
Ethanol	790	1.3	23	3.4×10^{-4}	26
Suspension	930	6.8	28	1×10^{-4}	76

needle, the flow rate was varied from 1 to 35 μL min^{-1}. The applied voltage between the needle and the ground electrode was varied up to 6 kV to establish the modes of EHDA processing of nHA suspension. A high speed camera was used to observe the cone and jet break-up process. At a chosen flow rate, the stable cone-jet mode was achieved within a range of applied voltage. Thus, the relationship between the applied voltage and flow rate for the suspension jetting in the stable cone-jet mode was established.

To investigate the influence of the distance between needle and grounded substrate, the needle of 300 μm in internal diameter was used. nHA suspension (6 wt.%) was syringed to the needle at a flow rate of 10 μL min^{-1}. The applied voltage between the needle and the ground electrode was set at 4–5 kV. The distance between the needle and the grounded titanium (99.6 wt.% pure, Advent Research Materials Ltd., Oxford, UK) substrate was varied from 10 to 40 mm. For the effects of flow rate and applied voltage on EHDA processing of nHA suspension, the distance between the needle (internal diameter of 300 μm) to substrate was kept at 20 mm.

2.3 Characterisation and comparison of nHA coatings

The morphology of nHA coatings was examined using field emission scanning electron microscopy (SEM, JEOL JSM/6310F) to understand the microstructural evolution. For SEM, the working distance was 15 mm and the accelerating voltage was set at 15 kV. The comparative study was based on the microstructural integrity and uniformity of the nHA coatings on Ti plates. The nHA coatings on the Ti plates were also characterized by X-Ray Diffraction (BRUCKER D8 DICOVER) to determine the phase composition. The scanning range was from 20° to 50°. The scanning period for the range was 900 s. The diffraction incident angle was set at 5° for thin coating scanning.

3 Results and discussion

3.1 nHA suspension characteristics

Ethanol is well known to give stable cone-jet mode electrohydrodynamic jetting and droplet generation, and its surface tension, electrical conductivity and relative permittivity are key parameters in achieving this. The density, viscosity, surface tension, electrical conductivity and relative permittivity of the 6 wt.% HA suspension were measured, as shown in Table 1. The ethanol content is an important parameter as it affects these properties, which in turn influences the electrohydrodynamic spraying. In comparison with ethanol, the presence of insulating nHA particles in the suspension has resulted in the trebling of the

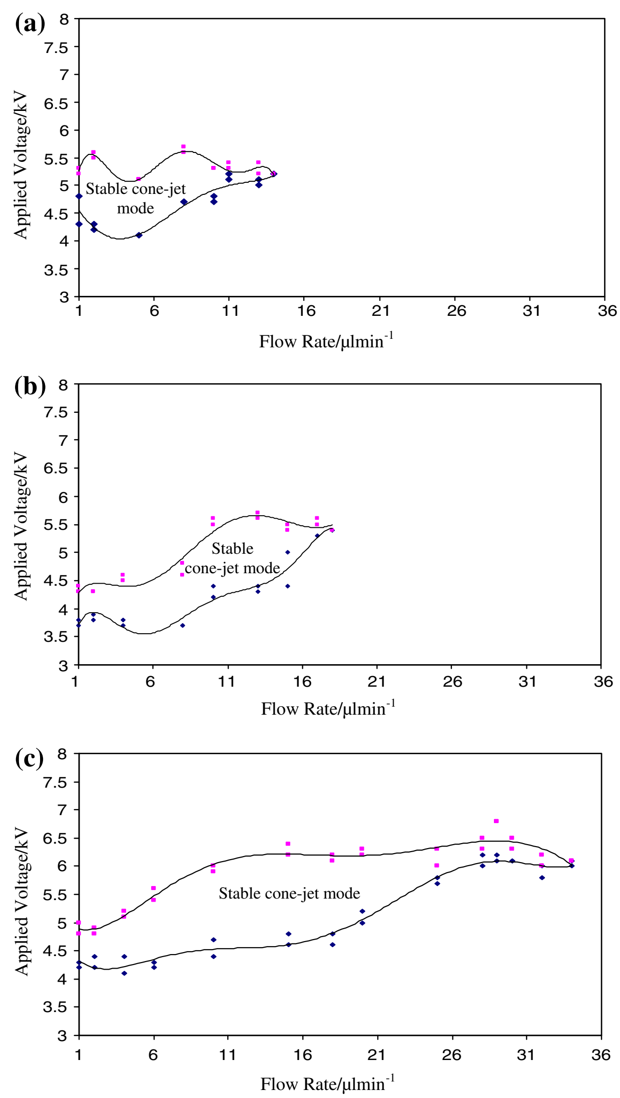

Fig. 2 Relationship between applied voltage and flow rate and the stable cone-jet mode envelope for the 3 wt.% nHA suspension by using needle orifice sizes of (a) 300 μm, (b) 500 μm and (c) 800 μm. The needle exit to substrate distance is 20 mm

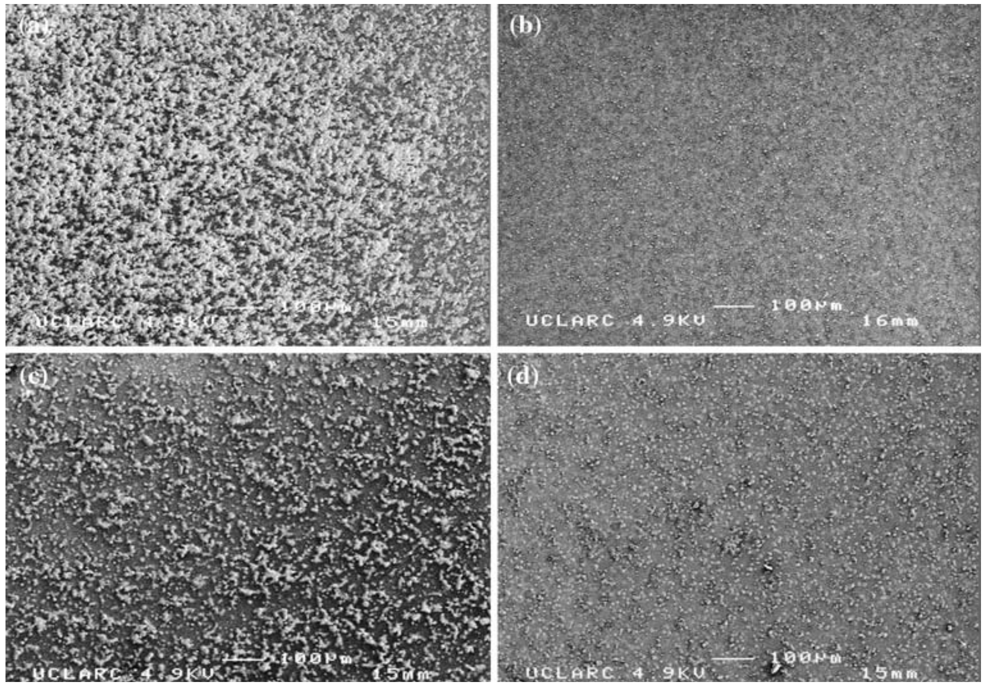

Fig. 3 Scanning electron micrographs of nHA coatings produced with the distance between the needle and substrate set at (**a**) 10 mm, (**b**) 20 mm, (**c**) 30 mm and (**d**) 40 mm

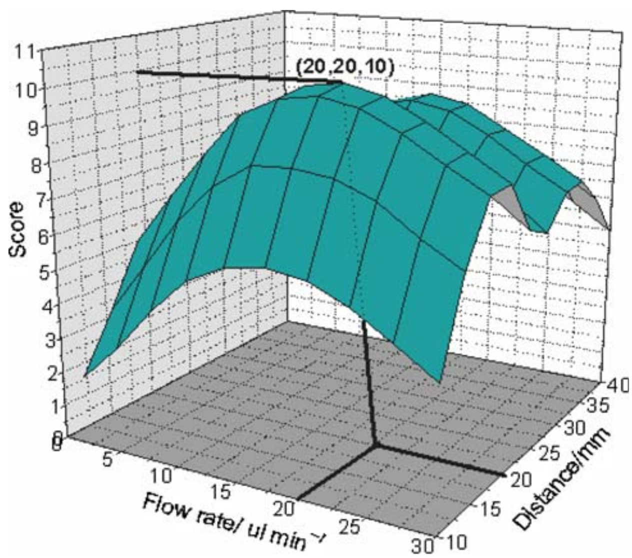

Fig. 4 The interrelationship of flow rate of suspension and distance between needle and substrate and quality score for nHA coating obtained by EHDA processing

relative permittivity, the reduction of the electrical conductivity by 1/3 and a fivefold increase in the viscosity. The last effect will result in the generation of coarser droplets during jetting [19]. The changes in electrical properties increase the electrical relaxation time and this parameter has to be smaller than the hydrodynamic time for classical EHDA to prevail [20]. However, jetting and droplet generation can be achieved from dielectric media [21].

3.2 EHDA spraying process and optimisation

To optimise the processing conditions of EHDA spraying of nHA suspension, the effects of needle size, the distance between the needle and grounded substrate, the suspension flow rate and the voltage applied were systematically investigated, as described below.

3.2.1 Effect of needle size

With increasing of the needle orifice size from 300 to 800 μm, the maximum flow rate for stable cone-jet mode jetting increased from 15 to 34 μL min^{-1}, as shown in Fig. 2a–c. Needle blockage was significantly reduced when increasing the needle size, although the applied voltage range for stable cone-jet mode decreased with a larger needle size at a high flow rate. It can be seen that the stable cone-jet map of EHDA processing of nHA suspension was susceptible to changes in the needle orifice size. Therefore, the needle orifice size can be used as a throughput control parameter for the coating process.

3.2.2 Effect of distance between the needle and grounded substrate

The morphology of nHA coating, when the distance between the needle and grounded substrate set at 10, 20, 30

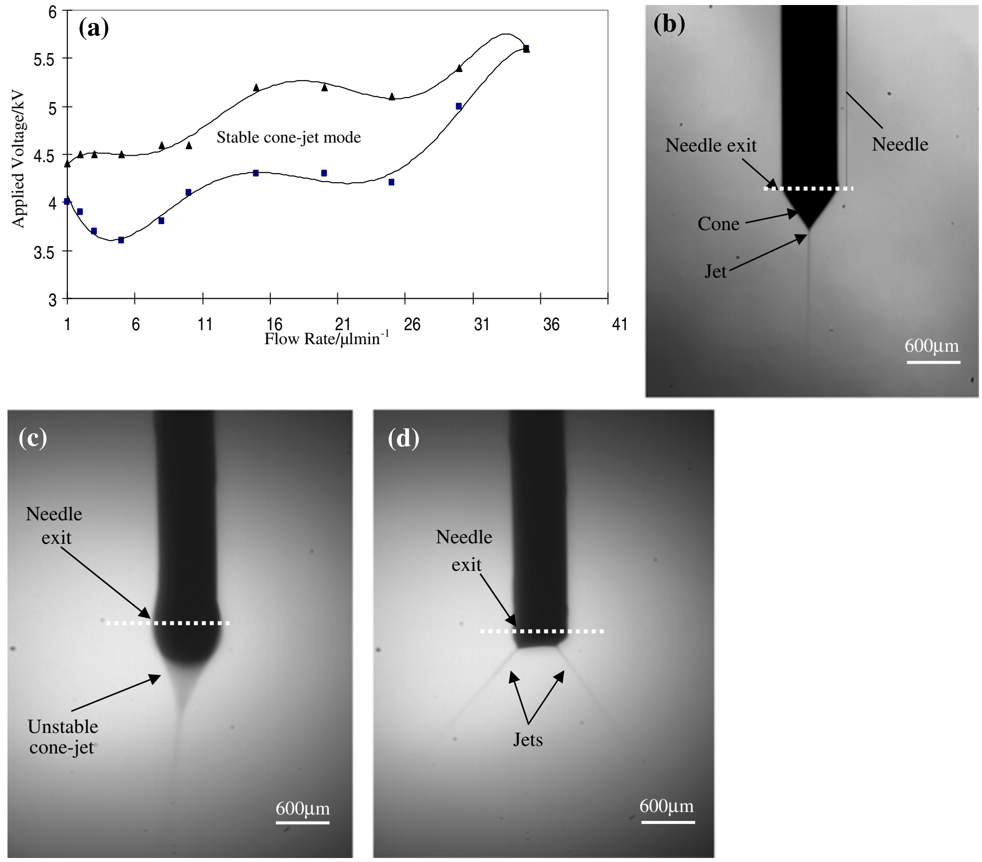

Fig. 5 (**a**) Relationship between applied voltage and flow rate for the 6 wt.% nHA suspension using a needle of 300 μm in internal diameter. Needle exit to substrate distance is 20 mm. The lowest flow rate which can be set with the present equipment is 1 μL min^{-1}. (**b**) Typical stable cone-jet mode obtained at 4.3–5.2 kV and 20 μL/min, (**c**) Unstable cone-jet mode and (**d**) Multi-jet mode

and 40 mm, is shown in Fig. 3. At short distance (10 mm), the nHA coating showed a rough texture (Fig. 3a). This is due to larger suspension droplets impinging on the substrate. With the increase of the distance, the nHA deposit became smoother due to the decrease of the suspension droplet sizes as evaporation of ethanol increased during transit. However, when the distance was set at 30 mm (Fig. 3c) and 40 mm (Fig. 3d), the substrate exhibited less nHA coverage compared with the coating produced with the distance set at 20 mm (Fig. 3b). Thus, the integrity of the nHA coating was greatly affected. The reason for that is there was insufficient liquid phase for the nHA particles to spread on the substrate after deposition. Therefore, among the chosen distances, 20 mm is considered as an optimised distance between the needle and the grounded Ti substrate. Compared with the coating set at 20 mm (Fig. 4b), the one at 30 mm (Fig. 3c) is much more non-uniform; however, the coating at 40 mm (Fig. 3d) presents some improvement.

3.2.3 Effect of flow rate

The morphology of the nHA coating produced varied with the increase of flow rate from 5 to 35 μL min^{-1}. At the lowest flow rate of 5 μL min^{-1}, the nHA coating was rougher in texture and covered only a part of the substrate. A low flow rate decreased the velocity of the suspension arriving at the needle outlet, and therefore affected the cone and jet formation and the subsequent droplets generation process during the jet break-up. The droplet size tends to be smaller at a lower flow rate [22] and this tends to make the coating more discontinuous. As flow rate was increased, the coating was continuous, however, at 30 μL min^{-1}, the coating produced was rougher, and more non-uniform. At 35 μL min^{-1}, the cone-jet became unstable, and a coating could not be prepared. Thus, a suspension flow rate of 20 μL min^{-1} resulted in the most uniform and integrated coating morphology.

To rank the effects of the flow rate and the distance between the needle and the substrate on EHDA processing of nHA suspension, the nHA coatings prepared under different conditions were scored according to the morphology achieved. A 3-D profile of the scores was established as shown in Fig. 4. This shows that the nHA coating produced with a flow rate of 20 μL min^{-1} and the distance of 20 mm achieved the top score. Therefore, to obtain a uniform and integrated nHA coating, these parameters should be used for this suspension. The coating surfaces shown in Fig. 3c and d correspond fairly well to the trough and peak immediately after the optimum, respectively, in Fig. 4. In fact, the conditions identified by the second peak are also favourable for coating, although not as good as the prominent optimum peak.

3.2.4 *Effect of applied voltage*

The relationship between the flow rate and applied voltage is crucial to achieve the stable cone-jet mode, which is essential for obtaining a continuous stream of suitable size droplets for uniform coating during spraying. The relationship between voltage applied and flow rate is shown in Fig. 5a and in this map the stable cone-jet mode (Fig. 5b) can only be achieved when the flow rate and the applied voltage are in a distinctive envelope. Otherwise, the unstable cone-jet mode (Fig. 5c) or the multi-jet mode (Fig. 5d) will be in operation. Therefore, for the 6 wt.% nHA suspension and the needle of 300 μm in internal diameter, the applied voltage need to be adjusted in the range of 4.3–5.2 kV when the optimised flow rate (20 μL min^{-1}) is in use. By changing the nHA content from 3 to 6 wt.% in the suspension, the stable cone-jet mode envelope shown in Fig. 5a changed considerably to that shown in Fig. 2a. This means that the flow rate regime increased from 15 to 35 μL min^{-1} and the applied voltage range became much wider. This makes process control operations much easier.

3.3 Surface morphology and microstructure of the nHA coating under optimised conditions

Using the 6 wt.% nHA suspension, a nHA coated Ti plate was produced using the optimised EHDA spraying parameters, which are a needle orifice size of 300 μm, a flow rate of 20 μL min^{-1}, the needle exit to substrate distance of 20 mm and the applied voltage of 4.3–5.2 kV. The entire coating exhibits a uniform, integrated morphology with nano-scale rod-like nHA particles (30–40 nm × 50–100 nm) as expected (Fig. 6a). The phase purity of HA was confirmed from the X-ray diffraction pattern of nHA coating on Ti (Fig. 6b). Only HA and Ti peaks were observed.

4 Conclusions

A procedure to optimise EHDA coating of titanium with nano-hydroxyapatite has been established in the current study. It was found that the needle orifice size, distance between the needle and substrate, the flow rate, the applied voltage and the nHA content had a very significant influence on the morphology of nHA coating prepared. The optimised processing parameters for a 6 wt.% nHA suspension were a needle orifice diameter of 300 μm kept at a distance of 20 mm from the substrate, a flow rate of 20 μL min^{-1} and the applied voltage kept within 4.3 kV and 5.2 kV. A uniform nHA coating was obtained under such conditions, and this is a crucial step forward in obtaining advanced nano-hydroxyapatite coatings of high quality for biomedical applications by using EHDA spraying.

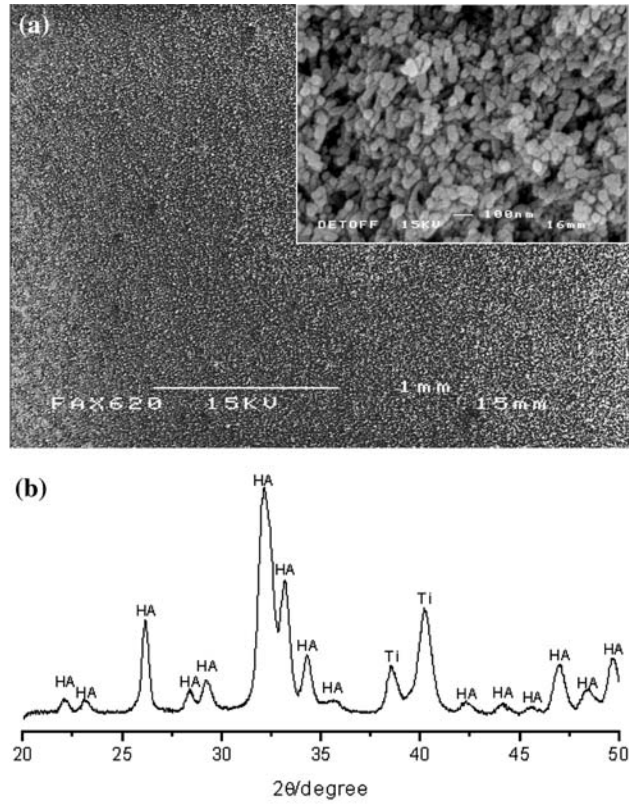

Fig. 6 (**a**) Scanning electron micrograph showing the microstructure of the nHA coating on the Ti substrate prepared using the optimized spraying parameters. (**b**) X-Ray diffraction pattern of the nHA coating prepared

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