

Electrophoretic deposition and characterization of nano-sized hydroxyapatite particles

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Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HAP), a major inorganic component of bone, has been used extensively for biomedical implant applications and bone regeneration due to its bioactive, biodegradable and osteoconductive properties [1–3]. However, the pure HAP is very brittle and its poor mechanical properties have limited its clinical applications. For this reason, a great deal of research concentrates on the development of HAP coatings and/or composites. Deposition of HAP coatings onto the surface of metal implants is a relatively recent development in clinical orthopaedics and has been achieved by a number of methods, such as plasma spraying [4, 5], dip coating [6], sputter coating [7], biomimetic coating [8], and electrophoretic deposition [9,10]. Plasma spraying [4] is the most developed process and thermally sprayed implants have been used in clinical practice for some years by now. However, plasma spraying, for extreme high temperatures of the plasma flame acting on HAP, results in the formation of resolvable molten phases. Unfortunately, they degrade in a short time after implantation, decreasing the adhesion of the HAP layer to the surrounding bone, as well as to the metal substrate. Furthermore, thermal spraying is a costly procedure and line-of-sight process, so it is not ideal for coating implants of complex shape or morphology.

Electrophoretic deposition (EPD) uses an applied electric field to deposit charged particles from suspension in a liquid onto a substrate, which acts as an electrode. The rate of deposition can be easily controlled by varying the applied current density or voltage and the composition of the deposited layer is determined by the composition of the particles in suspension. EPD is a low-cost, simple, non-line-of-sight and flexible ceramic coating process, and it can be used to deposit coatings on substrates of complex shape or surface morphology. Previous research demonstrates that EPD is an attractive method for formation of biomedical implants and a number of advantages and important possibilities of this method have been suggested [10]. Just like many other ceramic coating techniques, EPD-coated implants need a subsequent densification stage. The main problem associated with this process is the difficulty in sintering of the coatings. High sintering temperature is required for densification of the green coatings [11]. Lower sintering temperature can lead

to weakly bonded and low-density coatings, whereas, higher sintering temperature can result in degradation of the metal substrate and decomposition of the HAP coating. Decomposition of the HAP coating is undesirable as it leads to an enhanced *in vitro* dissolution rate [9]. A recent study has demonstrated that, to minimize degradation of the metal substrate and decomposition of the HAP coating, densification temperatures ideally should be below 1000 °C [12].

Many studies have experimentally found that dense ceramic parts can be achieved at a sintering temperature lower by several hundred degrees Celsius for nano-sized powders than for coarse powders [13]. The present author recently developed a novel technique to fabricate dense and crack-free ceramic composite coatings using ultrafine ceramic powders at low sintering temperatures [14, 15]. Thus the size of the HAP particles to be deposited by EPD is important. The use of nano-sized HAP powders can minimize the HAP coating densification temperature.

Since the EPD technique utilizes the phenomenon of the movement of colloidal particles suspended in a medium using an applied electric field, the choice of a suitable suspension medium is important in order to effectively disperse the nano-sized particles and to produce a colloidally stable suspension. The suspension medium used to suspend the particles during electrophoretic deposition must have a dielectric constant that gives effective coating characteristics and nanoparticles must be stable in that colloidal medium. There have been relatively few studies of the electrophoretic deposition of nano-sized HAP particles onto metal substrates [16]. Since the natural bone is a composite mainly consisting of nano-sized, needle-like HAP crystals and collagen fibers, this work is aimed at the preparation of HAP coatings onto titanium substrates by EPD from nano-sized HAP particles, and the choice of a suitable suspension medium is especially interesting.

In this study, nano-sized HAP particles which were synthesized in an aqueous mixed solution of $\text{Ca}(\text{NO}_3)_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$ with a stoichiometric ratio of Ca to P (=1.67) [17] were used to produce a suspension. Butanol, ethanol, isopropyl alcohol, and acetic anhydride were used as suspension media respectively. The powder concentrations were in the range of 5–10 g·l⁻¹. All

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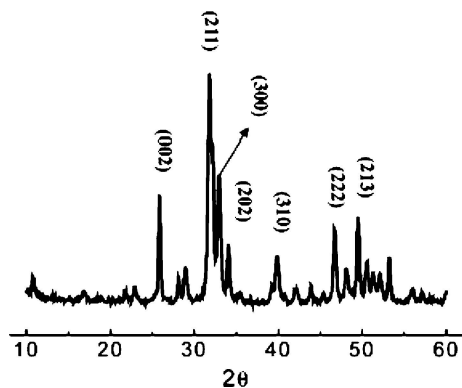


Figure 1 XRD spectra of HAP nanoparticles.

suspensions were subjected to ultrasonic agitation for several hours before use.

EPD was carried out by passing a d.c. electric current between a platinum counter electrode (anode) and a titanium substrate (cathode), distance between electrodes 20 mm, in a suspension at room temperature using applied voltages in the range of 50–200 V and deposition times of 0.5–5 min. After deposition the green form coatings were dried at room temperature in air and then sintered in a furnace at 800–900 °C for 2 h with Ar atmosphere at a heating rate of 3 °C/min and cooling rate of 2 °C/min. The phases and microstructure were examined using X-ray powder diffraction (XRD) (Rigaku Rotaflex D/max–C) and scanning electron microscopy (SEM) (Hitachi S-520). The HAP powder size was observed by transmission electron microscopy (TEM) (JEM-100CX II).

Fig. 1 shows the XRD spectra of the as-prepared HAP nanoparticles. The XRD pattern was verified as hydroxyapatite by the Powder Diffraction File (PDF Card No. 9-432). There is an extensive degree of peak broadening in the X-ray diffraction pattern due to the ultrafine nature of the powder.

Fig. 2 shows a TEM micrograph of the HAP powder. The size of the particles is about 20–30 nm in width and 50–60 nm in length.

The green coatings were fabricated by the accumulation of nanoparticles from a suspension on a titanium substrate by a dc field, various suspension media were chosen to effectively disperse HAP nanoparticles and to produce a colloidally stable suspension. Suspensions

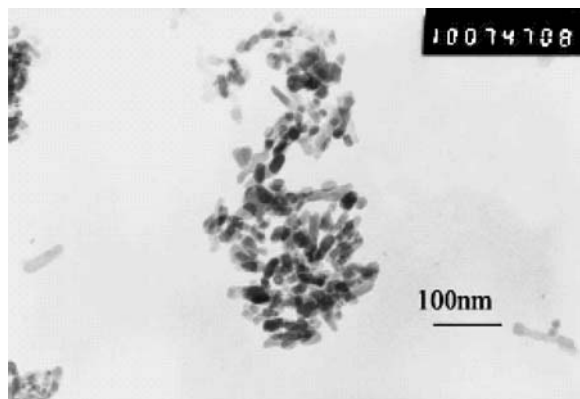


Figure 2 TEM photograph of HAP nanoparticles.

TABLE I Effects of solvent on the quality of HAP green coatings prepared by EPD

Solvent	Without or with HCl	pH	Stability of suspension	Quality of coating
Acetic anhydride	Without	4.5	Stable	Uniform
Ethanol	Without	7	Unstable	No deposition
	With	4.5	Unstable	No deposition
Butanol	Without	7	Unstable	No deposition
	With	4.5	Stable	Many cracks
Isopropyl alcohol	Without	6.5	Unstable	Deposited scarcely
	With	4.5	Stable	Many cracks

containing 10 g·l⁻¹ HAP nanoparticles were prepared using ethanol, butanol, isopropyl alcohol, and acetic anhydride as suspension media respectively. The deposition results showed that the quality of the HAP green coatings prepared by EPD depended strongly on the solvents used. Effects of the solvents on the quality of HAP green coatings after 1 min deposition using an applied voltage of 50 V are summarized in Table I. The HAP nanoparticles were deposited scarcely when butanol or isopropyl alcohol was used as solvent respectively. Although the addition of a very small amount of 1 mol/L HCl can improve the stability of suspension, the green coatings deposited were non-uniform in thickness and had many cracks. The suspension was unstable and there was no deposition with or without HCl when ethanol was used. Therefore, these solvents were unsuitable for the preparation of uniform and dense nano-sized HAP green coatings. However, nano-sized HAP green coating which was uniform in thickness and of good quality was easily obtained when acetic anhydride was used. The suspension using acetic anhydride as solvent was colloidally stable and the pH of the suspension was about 4.5 in the absence of HCl, and HAP nanoparticles were suitable for electrophoresis. So acetic anhydride was suitable for the preparation of dense and uniform nano-sized HAP coatings by EPD.

Fig. 3 shows an SEM image of the surface morphology of nano-sized HAP green coating electrochemically deposited on a titanium substrate from acetic anhydride suspension using an applied voltage of 50 V for 1 min. It can be seen that homogenous and densely

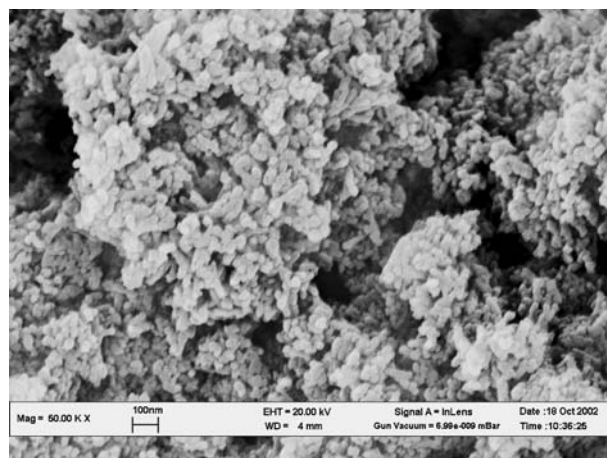


Figure 3 SEM image of HAP green coating.

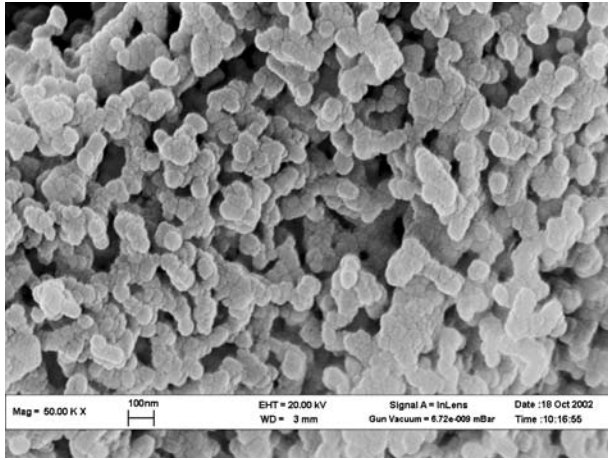


Figure 4 SEM image of HAP sintered coating.

packed nano-sized HAP particles (with the original particle size) were obtained in this process, which enabled the HAP green coating to achieve a high density at a relatively low sintering temperature, such as below 1000 °C.

The as-prepared nano-sized HAP green form was dried at room temperature in air and then sintered in a furnace at 850 °C for 2 h with Ar atmosphere. Fig. 4 shows an SEM image of the surface morphology of nano-sized HAP coating after sintering. It can be observed that the sintered coating was uniform, well-densified and fracture-free with particle sizes of mostly 50 nm in diameter.

In conclusion, nano-sized HAP particles were electrophoretically deposited onto titanium substrates followed by sintering processes. The choice of a suitable suspension medium is important to effectively disperse the nanoparticles and to produce a colloidal stable suspension. The homogenous and densely packed nano-sized HAP green form was deposited using acetic anhydride as suspension medium, which produced a uniform, well-densified and fracture-free nano-sized HAP coating at a relatively low sintering temperature

(800–900 °C). The further study of biomedical and mechanical properties of these nano-structured HAP coatings is ongoing.

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