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Electrophoretic deposition of silicon substituted hydroxyapatite coatings from n-butanol–chloroform mixture

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Abstract Silicon Substituted Hydroxyapatite (Si-HA) coatings were prepared on titanium substrates by electrophoretic deposition (EPD). The stability of Si-HA suspension in n-butanol and chloroform mixture has been studied by electricity conductivity and sedimentation test. The microstructure, shear strength and bioactivity in vitro has been tested. The stability of Si-HA suspension containing n-butanol and chloroform mixture as medium is better than that of pure n-butanol as medium. The good adhesion of the particles with the substrate and good cohesion between the particles were obtained in n-butanol and chloroform mixture. Adding triethanolamine (TEA) as additive into the suspension is in favor of the formation of uniform and compact Si-HA coatings on the titanium substrates by EPD. The shear strength of the coatings can reach 20.43 MPa after sintering at 700 °C for 2 h, when the volume ratio of n-butanol: chloroform is 2:1 and the concentration of TEA is 15 ml/L. Titanium substrates etched in H_2O_2/NH_3 solution help to improve the shear strength of the coatings. After immersion in simulated body fluid for 7 days, Si-HA coatings have the ability to induce the bone-like apatite formation.

Introduction

It is well recognized that apatites are found as calcified deposits in biological systems and geological minerals. The studies carried out by Carlisle [1] indicated the importance of the silicon on bone formation and calcification. The use of silicon-substituted hydroxyapatite (Si-HA) as a biomaterial has been reported recently [2–9]. In vivo testing has shown that the addition of Si during the HA synthesis leads to an improvement of the bioactive behavior [10–15]. In order to extend its usage to major load-bearing applications such as artificial hip replacement implants, it has been proposed that material could be used in the form of a coating on implant surfaces [16–19].

Deposition of bioactive coatings of hydroxyapatite (HA) onto the surface of metal implants is a relatively recent development in clinical orthopaedics [20]. These bioactive surface films are typically tens of micrometers thick. Thermal spraying [21] is the most developed process for depositing these HA coatings and thermally sprayed implants have been used in clinical practice for some years now. Thermal spraying is a costly procedure and it is a line-of-sight process and is therefore not always ideal for coating implants of complex shape or morphology(mesh, macropore, et al.).

Electrophoretic deposition (EPD) is a low-cost flexible coating process, and being a non-line-of-sight coating process, it can be used to deposit uniform coatings on substrates of complex shape or surface morphology. Furthermore, EPD can produce coatings of a wide range of thicknesses, from <1 mm to >100 mm, with a high degree of control over coating thickness and morphology [22]. As for many other ceramic coating techniques, EPD coated implants need a subsequent densification stage in order to sinter the coating. Wei et al. [23] reported a nano-particulate dual-coating approach to electrophoretic deposite HA coating on metal substrates, and research the interfacial bond strength of the coatings. Hamagami et al. [24] fabricated highly ordered macroporous apatite coating onto

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titanium by electrophoretic deposition method. Unfortunately, such coatings deposited by electrophoretic technique initially have the major drawback of poor adhesion and need for a post treatment to improve the adhesion, however the different in thermal expansion gave rise to generation of crack on the surface of coated layers or at the interface between the coatings and substrates during cooling after sintering [23]. Therefore, relatively low sintering temperature is desirable for the HA coated metal system. Previous studies have demonstrated that well-dispersed particles are necessary to produce densely packed deposits [25, 26]. On the contrary, aggregates form loosely bound structures, with low green densities and poor sintering behavior. Therefore, it is highly desirable to produce stable suspensions containing fine HA particles. As previously pointed out, the choice of a suitable medium is important for EPD.

Although HA coatings on titanium substrates have been prepared by thermal spraying, EPD, and others technology [16–19], the study of depositing Si-HA coatings onto metallic surface have few reported. So far, only Thian et al. [27] reported a study of magnetron co-sputtered Si-HA coating on a metallic substrate of thickness 600 nm with a Si content of approximately 0.8 wt%. The purpose of the present work was to fabricate densely packed Si-HA coating on titanium substrate by EPD in a high stable suspension containing fine Si-HA particles using n-butanol and chloroform as medium and triethanolamine(TEA) as the additive. The microstructure, chemical composition, thermal stability, interfacial shear strength and bioactivity in vitro of Si-HA coating were investigated.

Experimental procedure

Si-HA powder preparation

The procedure for preparation of Si-HA powders was based on that previously described [28]. The Si-substituted hydroxyapatite were prepared by hydrothermal method using $Ca(NO_3)_2 \cdot 4H_2O$, $(NH_4)_3PO_4$ and $Si(OCH_2CH_3)_4$(-TEOS) solutions as reagents. The pH of $Ca(NO_3)_2$ solution was keep higher than 10.0 and $(NH_4)_3PO_4$ solution was keep higher than 11.0 by the addition of NH_3 solution. A 0.025 M solution of $Ca(NO_3)_2 \cdot 4H_2O$ containing 0.2 g polyethylene glycol was added to $(NH_4)_3PO_4$ and TEOS solutions, and the mixtures were stirred for 0.5 h, then hydrothermal treatment at 200 °C for 8 h, following the chemical reaction:

$$10Ca^{2+} + 5.73PO_4^{3-} + 0.27SiO_4^{4-} + 1.73OH^- \\ = Ca_{10}(PO_4)_{5.73}(SiO_4)_{0.27}(OH)_{1.73}$$

The resulting precipitates were filtered, dried at 100 °C overnight. The weight percentage of silicon of Si-HA powder is 0.74% [28].

Electrophoretic deposition

Suspensions for electrophoretic deposition were prepared by ultrasonic agitation of Si-HA powders in n-butanol and chloroform mixed solution containing TEA as the additive in a 50 kHz ultrasonic bath for 60 min, and then the suspensions can be used to EPD without further aging. The Si-HA concentration in suspensions was 20 g/L. The electricity conductivity of the suspension was determined by a conductivity meter (Shanghai Precision & Scientific Instrument Co. Ltd., China) as a function of the concentration of TEA. For sedimentation tests, the suspensions with different concentration of TEA were poured into a 20 ml glass-stoppered graduated cylinder. The suspensions were then allowed to settle for 30 days, and then recorded by a digital camera.

Titanium sheets of 99.9% purity and dimensions of 10 mm × 10 mm × 0.5 mm were used as working cathodic electrode for EPD, and two platinum foil served as two counter electrodes. Before deposition, the titanium was degreased with acetone and ethanol in an ultrasonic bath, and washed with distilled water and then etched in 1:1(volume ratio) H_2O_2/NH_3 solution at room temperature overnight and dried in air at room temperature. EPD were performed at 30 V for 90 s. The distance between the electrodes was 7.5 mm. The coatings obtained were dried in an oven at 60 °C for 8 h and then sintered at 700 °C for 2 h in air.

In vitro bioactivity tests

The Si-HA coating was soaked in 25 ml of simulated body fluid (SBF) solutions at a pH of 7.4 at 37 °C for 7 days. The fluid was prepared by dissolving reagent-grade NaCl, KCl, $K_2HPO_4 \cdot H_2O$, $MgCl_2 \cdot H_2O$, $CaCl_2$, and Na_2SO_4 into distilled water and buffered to pH 7.4 with tri[hydroxymethyl]aminomethane $[(CH_2OH_3)_3CNH_3]$ and hydrochloric acid, as reported in literature [29].

Characterization of Si-HA coatings

The morphologies of Si-HA powders were observed by Hitachi 600 transmission electron microscopy (TEM) at 100 kV.The morphology of substrates and coatings were characterized by Philips XL30 Environmental Scanning Electron Microscope (ESEM) equipped with Philips Energy Dispersive X-ray Analyzer (EDX); the microstructure were characterized by Philips X'Perd MPD X-ray diffractometer system (XRD) using CuKα radiation at 40 kV and 30 mA, date sets were collected over the range of 5–90° with a step size of 0.02° and a count rate of 3.0°/min, the chemical composition were recorded using Nicolet Avatar 360 Fourier transform infrared spectroscopy(FTIR) in the 400–4,000 cm^{-1} range, at 4 cm^{-1} resolution averaging 64 scans; the interfacial shear strength of the coatings were measured by computer controlled electronic testing machine using a standard tensile adhesion test (ASTM-F1044). For each testing material, five specimens were used, and the shear strength data was reported as the average value.

Results and discussion

The effect of additive on the stability of suspension

In order to obtain the uniform and compact coating, the size of the particles must be fine enough to remain in suspension during the EPD process. The TEM morphology of Si-HA particles prepared by hydrothermal method was shown in Fig. 1. It shows that the Si-HA crystals display rod-like morphology with the length of about 20–50 nm and the diameter of about 5–10 nm. It also can be found that Si-HA nanorods are relative straight, and their surfaces are smooth, and Si-HA nanorods are relatively independent without associating with one another.

Furthermore a moderate electrophoretic mobility is expected for the whole process of deposition. Fast deposition rate is not beneficial for forming a uniform coating. On the contrary, it will result in deposits spalling and cracking. In a certain range, electricity conductivity is proportional to the ionic strength in the suspension, can affect the deposition rate [30]. This is because the electrophoretic motion of the particles towards an oppositely charged electrode are driven by the motion of the charges adhered onto the particles' surface. If there are only very few ionic charges available, they will not have sufficient force to move the particles. Usually people may obtain the appropriate deposition rate by the addition of acid or alkali as the additive in the suspension to adjust electricity conductivity.

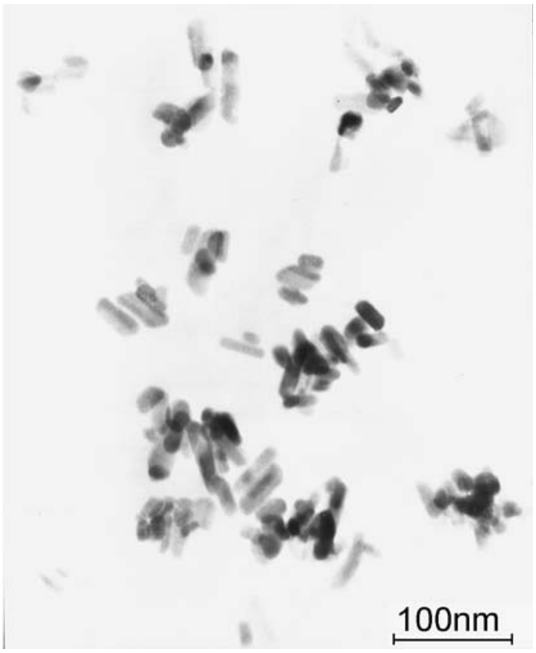


Fig 1 TEM morphology of Si-HA powder

In this experiment we use TEA as additive. Figure 2 shows the relation of electric conductivity with the concentration of TEA in 2:1 volume ratio of n-butanol and chloroform mixture and suspension. The conductivity of medium is 0.1 μs cm^{-1} approximately, and the conductivity of suspension is 0.2 μs cm^{-1} without adding TEA as additive. It indicated that there is interaction between Si-HA particles and the n-butanol. In n-butanol, ionization yields a protonated alcohol ($C_4H_9OH_2^+$) and an alkoxide ion ($C_4H_9O^-$). Si-HA particles, being basic in nature, adsorb an undissociated alcohol molecule onto their surface. This adsorbed alcohol ionizes into a protonated alcohol and an alkoxide ion. The protonated alcohol dissociates, thereby leaving the proton on the particle surface. The dissociated alcohol and the alkoxide ion desorb into the solution, leaving the particle positively charged in suspension: $P + C_4H_9OH = PH^+ + C_4H_9O^-$ (P: Si-HA particles), therefore, the conductivity of the suspension increases from 0.1 μs cm^{-1} to 0.2 μs cm^{-1} after the addition of Si-HA particles. With the increase of the concentration of TEA, the conductivity of suspension increases much rapidly than that of medium. This indicated that Si-HA particles not

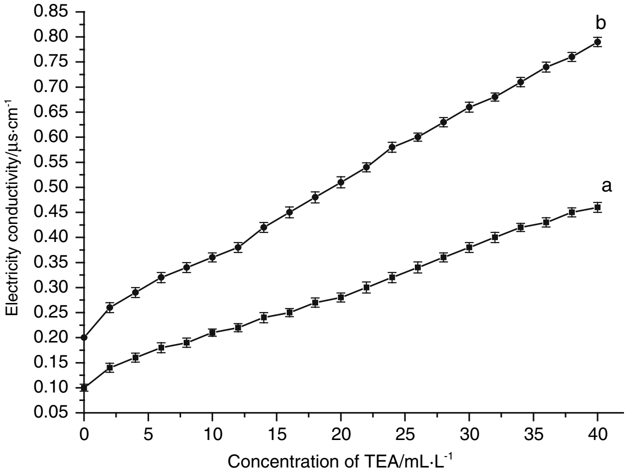


Fig 2 Relation of electric conductivity and the concentration of TEA. (**a**) medium + TEA; (**b**) suspension + TEA

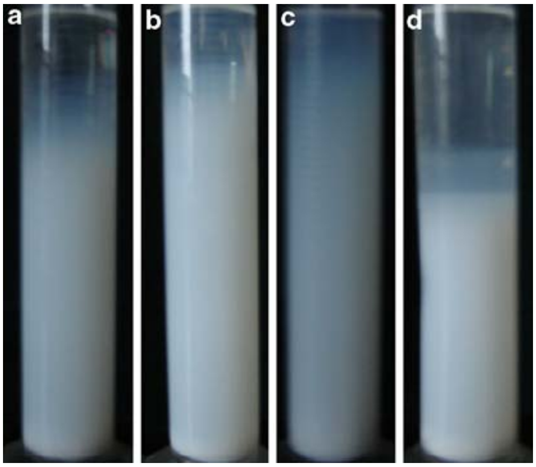


Fig 3 Stability of suspension with different concentration of TEA. (**a**) 0 mL L^{-1}; (**b**) 15 mL L^{-1}; (**c**) 30 mL L^{-1}; (**d**) 60 mL L^{-1}

only promote the n-butanol ionization, but also promote the TEA ionization. TEA has three -OH group, similar to n-butanol, can be adsorbed and ionized on the surface of the basic Si-HA particles too, so the conductivity of suspensions increase with the amount of TEA: $3P + N(C_2H_4OH)_3 = 3PH^{+} + N(C_2H_4O)_3^{3-}$. So, the addition of TEA is in favor of the stable suspension for EPD.

Stable suspension ensures the homogeneous of suspension and makes the quantity of EPD of Si-HA particles more than that of settling at the same time. It is important to note that the electricity charge of particles are favorable to the stabilization of suspensions for EPD only in a certain range. In order to determine the optimum concentration of TEA in suspension, the effect of concentration of TEA on the stabilization of suspension were investigated through sedimentation experiment. Fig. 3 shows the photograph of suspension with 20 g/L Si-HA and different concentration of TEA after settling for 30 days. The results clearly show that that there is a increase tendency in stability of the suspension when the concentration of TEA increasing from 0 to 30 mL/L and then decrease when the concentration of TEA exceed 60 mL/L. The quantity of electric charge of particles, solvation and Brownian movement are the three important factors of the stabilization of suspension. The addition of TEA increases the quantity of electric charge of particles as stated above. The aliphatic chains of TEA also act as steric barrier that result in repulsive potential energy between the particles higher than attractive potential energy, preventing the coagulation of particles owing to mutual collisions caused by Brownian movement [31], and improving the suspension stability. However owing to the three -OH groups of one TEA molecule, excessive TEA addition may led to the bridging between two particles and go against the dispersion.

Figure 4a and b show SEM images of the surface morphology of Si-HA coatings deposited on titanium substrate from suspension with or without adding 15 ml L^{-1}TEA as dispersant using an applied voltage of 30 V for 90 S after sintering at 700 °C for 2 h. With adding TEA as dispersant, it can be seen that the Si-HA coating was a crack-free and densely packed coating. Without adding TEA as dispersant, it can be seen that the coating was not densely packed and the coating has some agglomerated Si-HA particles. This further indicates that TEA as dispersant was effective in breaking up the agglomerates to produce a stable suspension.

The effect of medium on the stability of suspension

Although the suspension of Si-HA particles in pure n-butanol was stable and its dispersibility was good, it can not produced good adherent Si-HA coatings on titanium

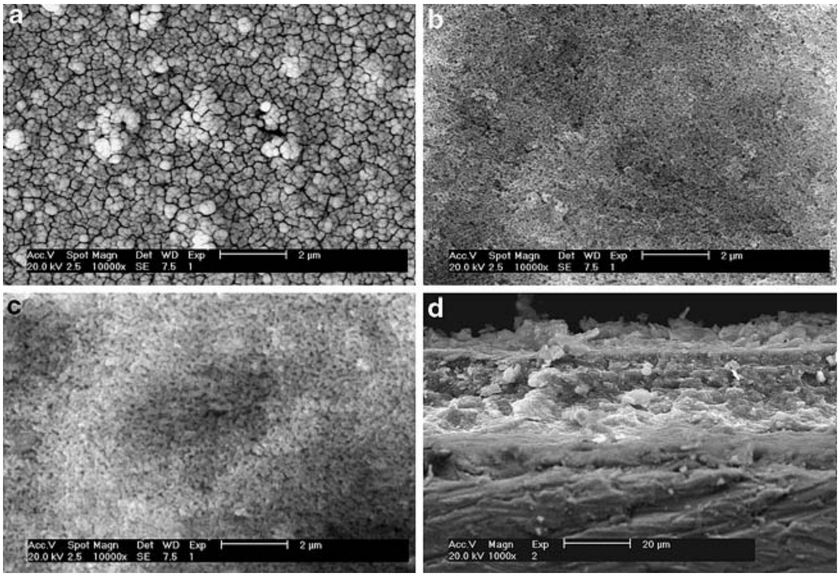


Fig 4 SEM morphologies of the coatings at different medium. n-butanol as medium: (**a**) without adding TEA; (**b**) with adding 15 mL/L TEA. n-butanol: chloroform (2:1) as medium: (**c**) with adding 15 mL/L TEA; (**d**) the cross section morphology of c

Table 1 Effect of different conditions on the shear strength of coatings

Substrate treatment	Sintering temperature(°C)		Medium				Shear strength (MPa)
	700°C	800°C	C_4H_9OH	$V_{C_4H_9OH}/V_{CHCl_3}$			
				8:1	4:1	2:1	
Untreated	√		√				8.4 ± 0.9
H_2O_2 + NH_3	√		√				15.30 ± 1.2
	√			√			16.30 ± 1.1
	√				√		19.93 ± 1.2
	√					√	20.43 ± 1.3
		√				√	16.46 ± 1.2

substrates [32]. In the present investigation it has been found that the presence of chloroform along with n-butanol helped to form a densely packed Si-HA coating on titanium substrates under a suitably adjusted electric field.

Figure 4b and c show the SEM micrographs of Si-HA coating in pure n-butanol and 2:1 volume ratio of n-butanol:chloroform mixture solution with 15 mL/L TEA as dispersant after sintering at 700 °C for 2 h. The two obtained coatings are compact and does not have the obvious crack. The thickness of coating deposited in n-butanol:chloroform mixture solution is about 50 μm (Fig. 4d). However when the volume of chloroform further elevates, the dispersibility and the electricity conductivity of the suspension reduced, therefore, the obtained coatings become thinner and more uniform.

The shear strengths between the coating and the metal substrate were shown in Table 1. It is found that the shear strength increase with the volume of chloroform increasing from 8:1 to 2:1. When the volume ratio of n-butanol:chloroform is up to 2:1, the shear strength between the coating and the substrate reach 20.43 MPa. That is to say, the shear strength of Si-HA coatings deposited in n-butanol-chloroform suspensions are higher than that in pure n-butanol suspensions. To obtained a good adherent coating, both adhesion of the particles with the substrate and cohesion between the particles are needed. It is well known [33] that polar solvents can substantially lower the surface energy of an oxide and are strongly attached to the surface, with a consequent lowering of the adhesion of other particles to the surface. The same is also valid in our case, as a thin layer of oxide is always present at the surface of the metallic titanium substrate and lots of –OH in the crystal lattice of Si-HA particles. However, in the presence of chloroform, the resultant polarity of the n-butanol-chloroform mixture is reduced, because of the low dielectric constant of chloroform, leading to reduction of the polar ends of n-butanol and consequently better adhesion of Si-HA particles on the titainium substrate and better cohesion between the particles from such suspensions. Therefore it is possible for obtaining a good adherent coating in n-butanol-chloroform suspensions.

Pretreatment of substrates

Owing to the module and component of hydroxyapatite are close to nature bone, the interfacial bonding strength between hydroxyapatite coatings and nature bone tissue is higher than that of between hydroxyapatite coatings and titanium substrates. Therefore, the interface between the hydroxyapatite coating and the titanium substrate surface becomes the weakest link in a chain. For Si-HA coating, as mentioned above, in addition to improving the adhesion of the particles with the substrate, pretreatment of titanium surface is also crucial. Before deposition, titanium surface always require to be pretreated to reduce the contamination, and improve the physical adsorption and mechanical embedded between the coatings and substrates. If the titanium surface is etched as serration appearance, which not only increase the interfacial bonding strength between the coatings and substrates but also may reduce the shear stress areas and transform shearing stress to compressing stress [34].

The surface of titanium substrates etched in H_2O_2/NH_3 solutions was shown in Fig. 5, a serration appearance was formed on the titanium surface. The formation mechanism can be described as follows:

$$H_2O_2 + OH^- = OOH^- + H_2O$$
$$Ti + OOH^- + 3OH^- = Ti(OH)_2O_2 + H_2O + 4e$$
$$Ti(OH)O_2 + 2H_2O = Ti(OH)_4 + H_2O_2$$
$$2OOH^- + 2Ti(OH)_4 = 2HTiO_3^- + O_2 \uparrow 2H_2O$$

The interfacial shear strength of the coatings before and after etched in H_2O_2/NH_3 solution are 8.5 MPa and 15.3 MPa, respectively (Table 1). It indicated that this coarse structure on the titanium surface can enhance the interfacial shear strength between the coatings and substrates effectively.

XRD and FTIR of the coatings

To improve the shear strength, the coatings must be subsequently densified by heating the coated implant to ele-

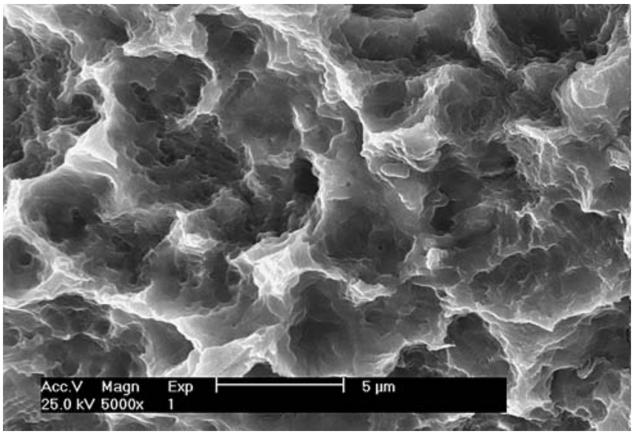


Fig 5 Surface morphology of titanium sheet after etched in H_2O_2/NH_3 solution

vated temperatures sufficient to sinter the Si-HA coating. Heating is problematic in terms of degradation of the Si-HA coating and deterioration of the metal substrates. XRD patterns of Si-HA powder and coating sintering at 700 °C and 800°C were shown in Fig. 6. As it can be seen, after heating at 700 °C, the patterns with no secondary phase are detected, XRD pattern of Si-HA coating is almost the same with as Si-HA powder, indicating no phase change during EPD and heating process. When the temperature reaches 800 °C, some rutile phase was detected, suggesting that titanium substrate has been oxidized to chemical stable rutile. The shear strength of the coatings is 20.43 MPa sintering at 700 °C, and 16.46 MPa at 800 °C (Table 1), indicating that layer of oxide on the titanium surface may reduce the adhesion between the coatings and substrates. Therefore, the sintering temperature should not exceed about 700 °C.

FTIR spectra of Si-HA powder and Si-HA coating were shown in Fig. 7. The bands at 3,571 and 631 cm^{-1} correspond to the stretching and vibrational modes, respectively, of the hydroxyl group. The bands at 874 cm^{-1} is assigned to Si-O vibration modes of SiO_4^{4-} groups. The doublet at 1,409, 1,457 cm^{-1} are assigned to CO_3^{2-} groups. The intense bands at 1,100, 1,034, and 965 cm^{-1} correspond to P–O stretching vibration modes, whereas the doublet at 572, 631 cm^{-1} corresponds to the O–P–O bending mode, Finally, the broad band at 3,420 cm^{-1}, as well as the band centered at 1,653 cm^{-1}, correspond to H_2O adsorbed on the surface.

Bioactivity of the coatings

SEM micrograph of Si-HA coating after immersion in SBF for 7 days is shown in Fig. 8. The surface of the coating is covered by a newly formed layer consisting of small granular structures. The chemical composition of the small granular were detected by EDX, the molar ratio of $n(\text{Ca})/n(\text{P}) = 1.60$, indicating that Si-HA coatings have the ability to induce the bone-like apatite nucleation and growth on their surfaces from SBF. Other authors have also observed similar findings in pure HA coatings. Bone-like apatite layer has been found to be important to establish the bone-bonding interface between bioactive materials and living tissues.

Fig 6 XRD patterns of Si-HA powder and coatings sintered at different temperature. (**a**) Si-HA powder; Si-HA coating: (**b**) before sintering; (**c**) sintering at 700 °C; (**d**) sintering at 800°C

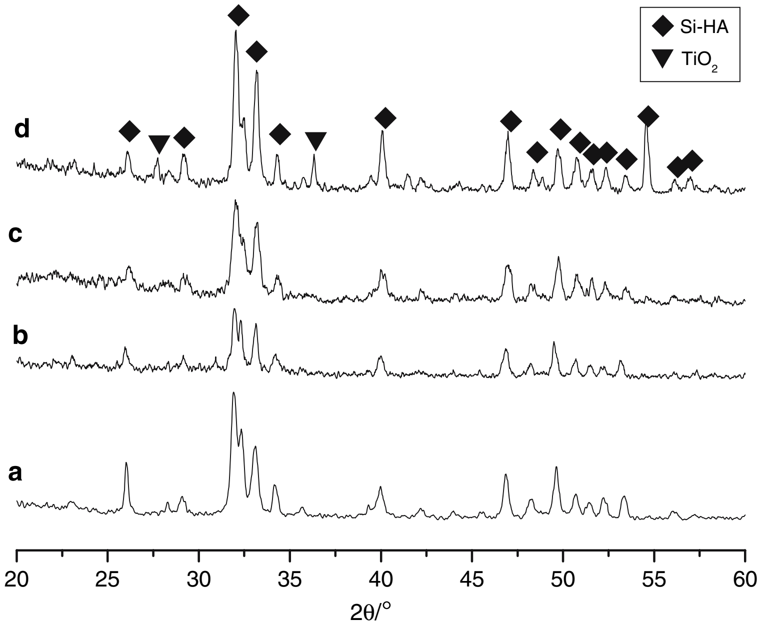
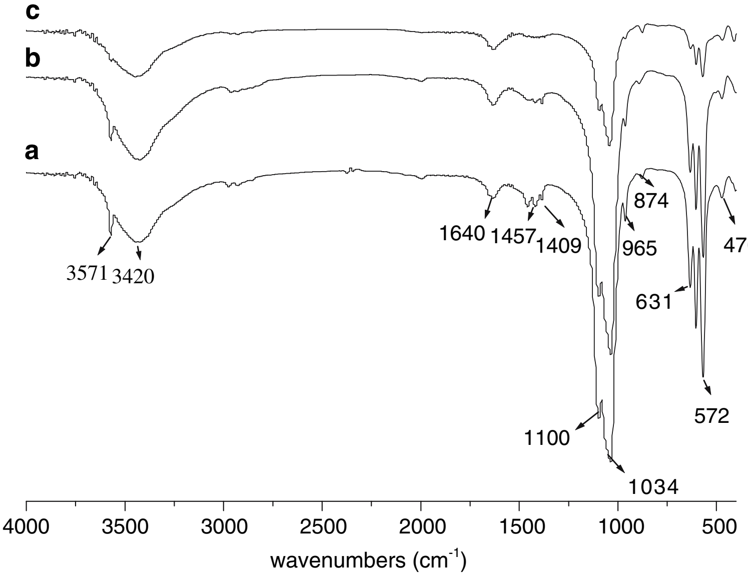


Fig 7 FTIR spectra of Si-HA powder and coatings. (**a**) Si-HA powder; Si-HA coating: (**b**) before sintering; (**c**) sintering at 700 °C



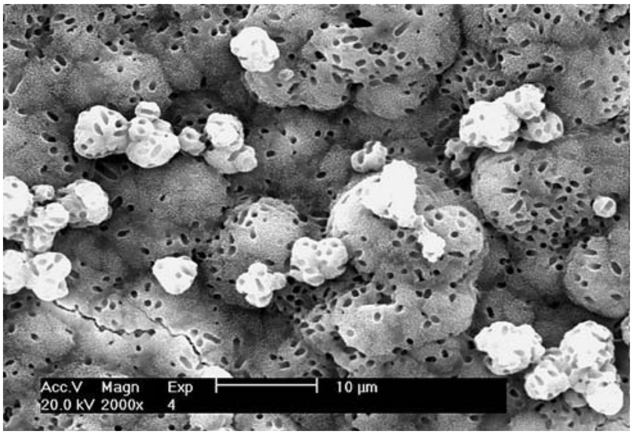


Fig 8 Surface morphology of Si-HA coatings after soaking in SBF for 7 days

Conclusions

Si-HA powders were prepared by hydrothermal method and electrophoretic deposited on titanium substrate. According the sedimentation and the shear strength tests, the n-butanol-chloroform mixture is found to be better than pure n-butanol for the Si-HA particles. The presence of chloroform along with n-butanol as medium helps to forms a densely and compact Si-HA coatings. When the volume ratio of n-butanol: chloroform is 2:1, the shear strength between the coating and the substrate reaches as high as 20.4 MPa. TEA as additive can improve the conductivity and dispersibility of the suspension. The suitable concentration of TEA is 15–30 mL/L. A serration appearance formed on the titanium surface after etching in H_2O_2/NH_3 solution, which increases the shear strength of the coatings effectively. The optimum heating temperature for Si-HA coatings should be controlled about 700 °C. SBF tests show that Si-HA coatings have good bioactivity.

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