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Electrophoretic deposition of hydroxyapatite nanostructured coatings with controlled porosity

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Abstract

Hydroxyapatite (HA) coatings with controlled porosity were prepared by electrophoretic deposition (EPD) method. Carbon black (CB) particles were used as the sacrificial template (porogen agent). Two component suspensions containing different concentrations of HA and CB particles were prepared in isopropanol. It was found that the finer and positively charged HA nanoparticles are heterocoagulated on the coarser and negatively charged CB particles to form CB–HA composite particles with net positive charge. The deposition rate from the suspensions with WR (C_{CB}/C_{HA} ratio) of 0.25 was faster than that of those with WR: 0.5 at initial times of EPD. However the situation was reversed at longer EPD times. It was also found that the amount of porosity in the coatings increases as the CB concentration in the suspension increases (15%, 24%, 31%, 43% for the coatings deposited from the suspensions with 20 g/L HA nanoparticles and 0, 5, 10 and 20 g/L CB particles, respectively).

Keywords: Carbon black (CB) particles; Electrophoretic deposition (EPD); Hydroxyapatite (HA) nanoparticles; Isopropanol; Porosity

1. Introduction

Porous ceramics have found applications in several fields such as biomaterials, filters, and optical materials.[1] Controlling the pore characterizations such as size, size distribution and shape is of great importance in these applications. Different processing techniques have been used to fabricate porous ceramic materials.[2] Colloidal processing has been used extensively to fabricate porous ceramics with highly controlled porous microstructures using polymeric or silica spherical particles as the sacrificial template (porogen agent) which are removed by either heat or chemical treatment.[3–5] Electrophoretic deposition (EPD) is a colloidal processing method which has been used to fabricate porous coatings on the metallic substrates using polymeric particles as the sacrificial template.[6–11] EPD is a two step process: in the first step charged particles are dispersed in a suitable liquid and migrate toward the electrode with opposite charge under the application of electric field; in the second step they deposit on the electrode and form a relatively dense layer of particles on it.[12]

Hydroxyapatite (HA) is the main inorganic part of human bone.[13] HA has high bioactivity, biocompatibility, biodegradability and osteoconductvity[14–16] making it an appropriate material for using in biomedical applications. However, HA has poor mechanical properties (for example low fracture toughness) limiting its usage in high load bearing applications. So usually HA is used in the form of coating on the biocompatible metals such as titanium and 316 L stainless steel and their alloys. Electrophoretic deposition (EPD) has been widely used to deposit HA coatings on the metallic substrates.[17–21] It has been reported in the literature that the porous structure of the HA coatings is necessary to implant fixation by bone ingrowths into their pores.[22–25] In the present work the economical fabrication of HA coatings with controlled porosity by EPD method has been reported. Carbon black (CB) particles have been used as the cost effective sacrificial template and the effect of their concentration on the EPD process as well as the porosity of obtained coatings have been discussed.

2. Experimental

2.1. Suspensions preparation

Hydroxyapatite (HA) nanoparticles were synthesized by metathesis method.[26] Carbon black (CB) powder was used as

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the sacrificial template. The zeta potential and particles size distribution of HA and CB particles were measured in isopropanol (Malvern instrument, Worcestershire, UK). The suspensions of HA nanoparticles (10 and 20 g/L) with different concentrations of CB particles (C_{CB}/C_{HA} ratio (WR): 0, 0.25, 0.5 and 1) were prepared in isopropanol. The suspensions were magnetically stirred and ultrasonically dispersed (Sonopuls HD 3200, 20 kHz; Bandelin Co., Berlin, Germany) for 24 h and 10 min, respectively. The electrical conductivity of the suspensions was measured against CB concentration (Cond 720, WTW series; Inolab, Weilheim, Germany). The zeta potential of particles was measured in two component (HA + CB) suspension (Malvern instrument, Worcestershire, UK).

2.2. Electrophoretic deposition

The plates of 316 L stainless steel with the dimension of 40 mm × 20 mm × 1 mm were used as the substrate as well as counter electrodes (only 20 mm × 20 mm of substrate was exposed to deposition and remainder of their surface insulated). The distance between two electrodes was 1 cm in EPD cell. EPD was performed at 60 and 200 V from the suspensions with different concentrations of HA and CB particles using a laboratory D.C. power supply (HY30002E; Huayi Electronics Industry Co., Hangzhou, Zhejiang, China). The current density during EPD was recorded using a computer connected digital multimeter (289 True RMS; Fluke, Everett, WA). The immersion weight (W_{imm}) of deposits was measured *in situ* according to the method described in Ref.[27] The wet weight (W_{wet}) of deposits prepared at 60 and 200 V for 15, 30, 60, 120, 240 and 360 s was measured immediately after EPD (GR-200 (0.1 mg accuracy); A & D Co., Tokyo, Japan). The wet density of deposits was calculated according to the Archimedes' principle:

$$\rho_{wet} = \frac{W_{wet}}{Vol_{wet}} \quad \text{and} \quad Vol_{wet} = \frac{W_{wet} - W_{imm}}{\rho_{ISP}} \tag{1}$$

where Vol_{wet} is the wet volume of deposit and ρ_{ISP} is the density of isopropanol (0.78 g/cm^3).

Thermogravimetric (TG) analysis was used to determine the temperature range where CB particles burn out completely as well as their amount in the deposits prepared from the suspensions with different concentrations of CB particles. The powders obtained from scratching the dried HA–CB composite coatings from the substrates were used as the samples for TG analysis. TG analysis was performed at the temperature range of 25–800 °C (heating rate: 5 °C/min).

The deposits were dried at room temperature in air overnight and then sintered. The temperature program for sintering process was determined using the data obtained from TG analysis. The temperature was raised from room temperature (25 °C) to 480 °C at the heating rate of 10 °C/min; then it was increased to 650 °C at the heating rate of 1 °C/min and was kept at this temperature for 30 min to complete the burning of CB particles; then temperature was raised to 700 °C at the heating rate of 5 °C/min and sintering was performed at this temperature for 1 h. The microstructure of deposits was observed by scanning electron microscope (SEM) before and after sintering. The amount of porosity in the coatings was determined by image analyzing (MIP software).

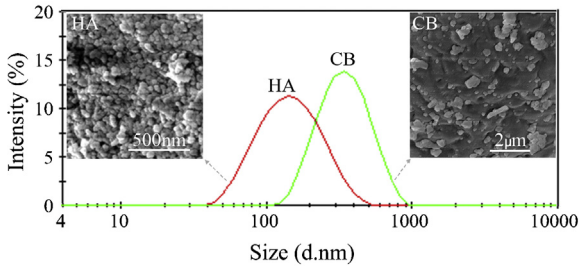

Fig. 1. Particles size distribution for HA and CB particles in isopropanol; the inset figures are the SEM images of HA and CB particles.

3. Results and discussion

3.1. Suspensions properties

The zeta potential of HA and CB particles in isopropanol was +37.4 and −15.23 mV, respectively. The results for particles size distribution of HA and CB particles are shown in Fig. 1. The SEM images of HA and CB particles are also shown as the insets in Fig. 1. As can be seen the majority of CB particles are larger than HA particles. The mean agglomerate size and the range of particles size distribution are 159.7 nm and 37.84–531.2 nm for HA nanoparticles, respectively; while these parameters are 364.3 nm and 122.4–955.4 nm for CB particles, respectively. The zeta potential of particles against CB concentration in two component suspension is shown in Fig. 2. As can be seen particles are positively charged and their surface charge decreases continuously with CB concentration. When CB particles are added into the suspension of HA nanoparticles in isopropanol, the composite particles of CB–HA with a net positive surface charge are generated by the heterocoagulation of finer and positively charged HA nanoparticles (with the higher

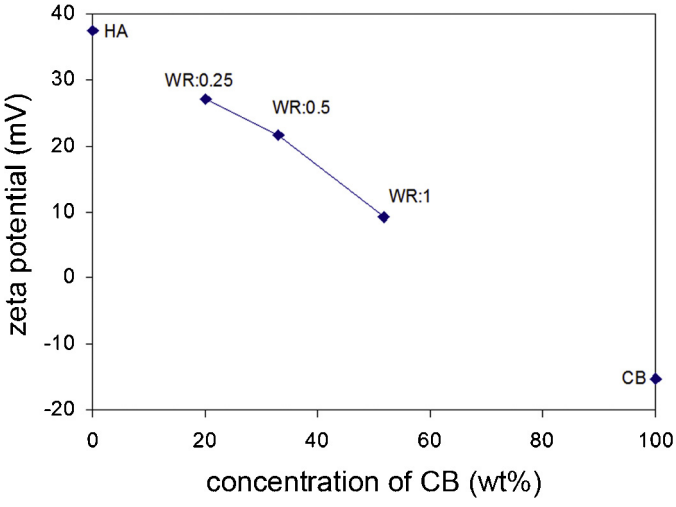

Fig. 2. Zeta potential of particles in two component (HA + CB) suspension as a function of CB concentration.