

Electrophoretic deposition of functionalized polystyrene particles for TiO₂ multi-scale structured surfaces

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Titanium is an interesting material for biomedical implants thanks to its physical and chemical properties. In particular, TiO₂ coatings with a surface characterized by micro-patterning combined with nano-topography are extremely attractive for orthopaedic implants in terms of enhanced osteointegration and consequently improved implant fixation. In the present work, a new method for the preparation of TiO₂ multi-scale structured coatings is presented. This method is based on three steps. Firstly, monodispersed polystyrene (PS) microsized beads are functionalized with TiO₂ submicron particles by a wet process involving a cationic polyelectrolyte. Secondly, the resulting TiO₂-PS composite particles in suspension are used to prepare coatings by electrophoretic deposition (EPD), a simple and flexible electrochemical technique. The EPD is performed cathodically, avoiding uncontrolled oxidation of the substrate. Finally, after removal of the PS spacers during the sintering process, TiO₂ coatings with a combined micro- and nano-topography are achieved from deposits thicker than 100 μm. This achievement presents two relevant aspects: potential applications of the multi-scale structured TiO₂ surfaces (particularly in the biomedical field); the simplicity and flexibility of the process used.

1. Introduction

Chemical and morphological properties of coatings for implants influence the biological response of the bone tissue surrounding the implant [1–4]. A favourable biological response corresponds to a bone remodelling with bone growth onto the implant surface (enhanced osteointegration). Outstanding physical and chemical properties such as high corrosion resistance and good biocompatibility make titanium an interesting material for biomedical implants [5]. In particular, TiO₂ coatings with a surface characterized by micro-patterning combined with nano-topography are extremely attractive for this application, favouring osteointegration at the bone-implant interface [4].

Electrophoretic deposition (EPD) is an established technique to obtain coatings and thick films [6]. EPD has been investigated as potential coating technique in the field of biomedical (orthopaedic and dental) implants [7–11]. For biomedical applications, cathodic EPD is preferred to anodic EPD because it avoids uncontrolled oxidation of the substrate [8]. In cathodic EPD, positively charged particles in suspension are driven by the effect of an electric field to the negatively charged electrode (cathode), forming a deposit on it.

In the present work, a new approach for the preparation of TiO₂ multi-scale structured surfaces on Ti6Al4V substrates is proposed, for potential application in the biomedical field (including research and development areas). This approach is based on three steps: functionalization of polystyrene (PS) particles with TiO₂ using polyelectrolytes; controlled cathodic EPD of PS-TiO₂ composite particles; final sintering of the coatings combined with the so called “negative template method”. The micro- and nano-surface features are expected respectively from the burning out of the PS spacers and the densification of the TiO₂ particles.

The procedure of colloidal particle functionalization aimed at cathodic EPD was the object of a recent publication [12]. In this previous work two methods for the preparation of suspensions with TiO₂-PS composite particles in isopropanol were developed. In both methods, submicron TiO₂ particles covered the surface of microsized polystyrene (PS) beads. The method based on the use of a polyelectrolyte was found to be superior in terms of more complete adsorption of the TiO₂ particles on the PS beads. Nevertheless in the authors' conclusions an improvement of that method was needed in order to obtain more uniform coatings with lower applied voltages and shorter EPD times. In the present study, we improve the method for the preparation of suspensions with TiO₂-PS composite particles based on the use of a polyelectrolyte. The improvement of the method is achieved mainly by changing suspension concentrations and by introducing new centrifugation steps with dispersion in different suspension media.

Abbreviations: EPD, Electrophoretic deposition; PS, Polystyrene; PDADMAC, Poly-diallyl dimethyl ammonium chloride.

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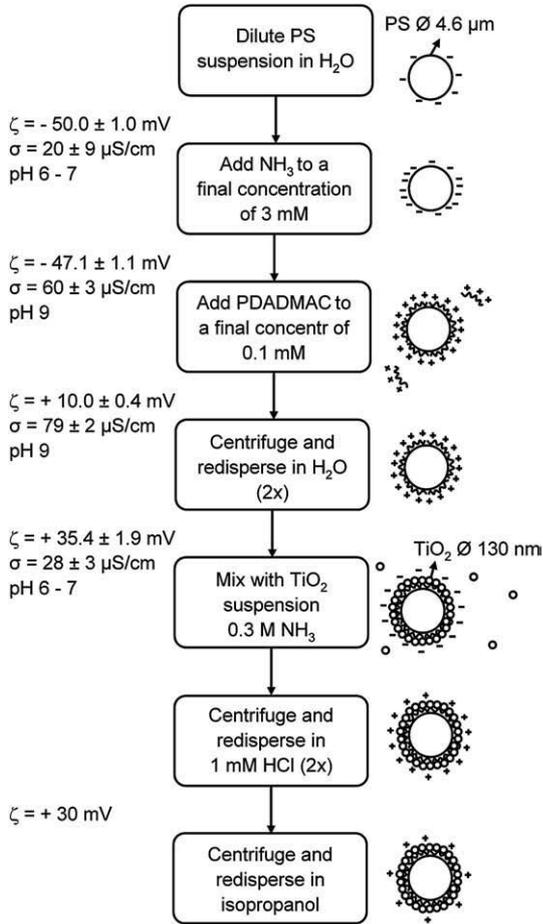


Fig. 1. Flow diagram illustrating the colloidal process used for the preparation of suspensions for cathodic EPD of TiO₂-PS composite particles, with indication of zeta potential, conductivity and pH values typically measured during the procedure.

The negative template method is based on the use of solid fugitive spacers. The removal of the solid spacer may occur thermally (sintering with burning out of polymeric spacers) or chemically (etching of polymeric or silica spacers). In the biomedical field, the negative template method has been applied for example in the preparation of titanium foams [13] and of highly interconnected porous YSZ ceramics and composites with interpenetrated phases of tricalcium phosphate/ hydroxyapatite and poly(DL-lactide-co-glycolide) [14,15]. Using the negative template method in combination

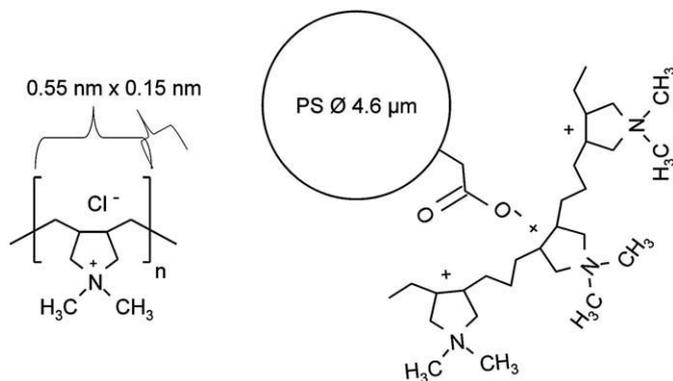


Fig. 2. Schematic illustration of the adsorption of the cationic polyelectrolyte PDADMAC (polydiallyl dimethyl ammonium chloride) on the surface of a carboxyl-modified PS (polystyrene) bead. Estimated dimensions of the monomer used for calculation of the PDADMAC optimal concentration are indicated on the left side drawing.

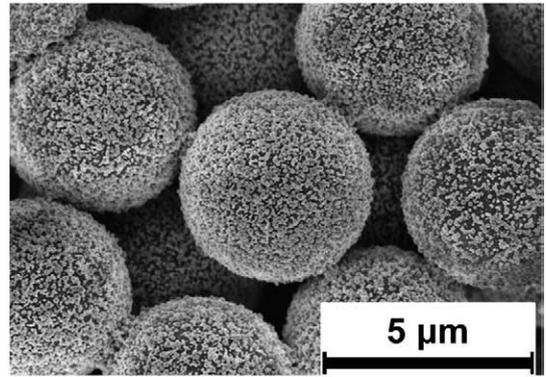


Fig. 3. Secondary electron SEM micrograph of TiO₂-PS composite particles deriving from the colloidal process of Fig. 1.

with EPD, Hamagami et al. prepared macroporous coatings on titanium substrates using ethanol suspensions with hydroxyapatite nanoparticles mixed with PS beads (3 µm in diameter) [16]. In the context of this paper, the work of Hamagami et al. proved the potentiality of EPD to prepare coatings with controlled morphology.

2. Materials and methods

2.1. Preparation of TiO₂-PS composite particles in suspension

Carboxylate-modified polystyrene beads of 4.6 µm in diameter were used as fugitive spacers. Titania (TiO₂) spherical submicron particles with an average diameter of 130 nm were used as coating material. A more detailed description of the particles has been already documented [12]. Polydiallyl dimethyl ammonium chloride (PDADMAC) solution with very low molecular weight ($M_w < 100,000$), 35 wt.% in water, was purchased from Sigma-Aldrich Chemie GmbH. The solvents used were isopropanol puriss. p.a. (Fluka Chemie GmbH), deionized water 18.2 MΩ cm (Milli-Q), and ammonium hydroxide solution puriss. p.a. NH₄OH, ≤25% in water (Fluka Chemie GmbH).

The optimized procedure of particle functionalization used for the preparation of suspensions for cathodic EPD of TiO₂-PS composite particles is given in the flow diagram of Fig. 1. Different initial dilution factors (10 or 100) and different starting volumes of the as received PS suspension (3 to 12 ml) resulted in final volume concentrations ranging from ca. 2 to 8 vol.% TiO₂-PS. In particular, the particle concentration of ca. 8 vol.% TiO₂-PS was obtained by initially diluting six independent volumes of the as received PS suspension (2 ml at 3.8 vol.% PS) of a factor of 10, proceeding with centrifugation, redispersion of the sediment in smaller volumes and mixing of suspension volumes to a final total

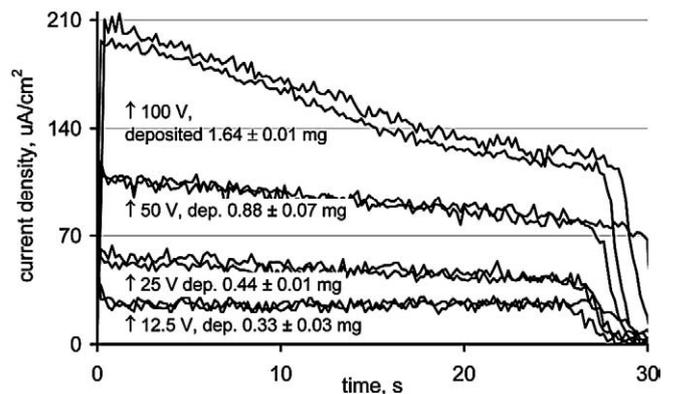


Fig. 4. Current evolutions measured during EPD tests at different voltages (12.5, 25, 50, 100 V) for 1 min. The distance between electrodes was 4 mm. TiO₂-PS composite particles dispersed in isopropanol according to the colloidal process of Fig. 1 were deposited on Ti6Al4V substrates. Corresponding values of deposited mass are indicated.

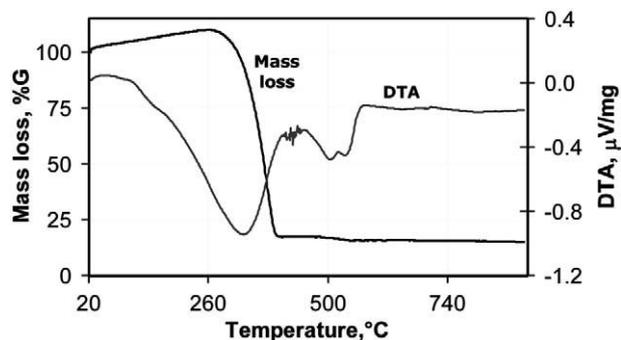


Fig. 5. Plot from the TG-DTA (Thermo Gravimetric-Differential Thermal Analysis) performed on a dried drop of PS suspension in oxygen atmosphere at 5 °C/min. The mass loss given by PS burning out started at ca. 260 °C and ended up at ca. 405 °C.

volume of 6 ml isopropanol. Fig. 1 also reports typical values of zeta potential, conductivity and pH measured during the preparation of one batch. Fig. 2 shows a schematic illustration of the adsorption of the polyelectrolyte PDADMAC on the surface of a carboxyl-modified PS bead, before mixing with the TiO₂ submicron particles.

Zeta potential and electrical conductivity were measured with a ZetaSizer Nano Z (Malvern Instruments Ltd.); pH was monitored using color-fixed indicator sticks (Roth). High resolution scanning electron microscopy (SEM Hitachi S-4800) was used to evaluate the produced composite particles. The suspension stability was evaluated by naked-eye observation over time of the suspension in a 12 ml centrifuge tube.

2.2. Cathodic EPD

The substrates consisted in Ti6Al4V disks, previously HF-etched to a surface roughness of $R_a = 0.1 \mu\text{m}$. The exposed area of the working electrode was ca. 0.12 cm². As counter electrode, a stainless-steel (316 L) disk was used with an exposed area of ca. 0.4 cm². The procedure for cleaning samples before the EPD experiments is published

elsewhere [12]. A special electrochemical cell of 5 ml volume was constructed in our laboratory for a controlled withdrawal of the sample from the suspension. The counter electrode was held at a fixed distance of 4 mm from the working electrode. Before the EPD, the cell was rotated to a vertical position so that the electrodes were immersed in the suspension. During the last 10 s of the EPD, the cell was turned back to the horizontal position so that the suspension was gradually removed from the exposed area of the sample.

EPD experiments were performed at constant voltage supplied by a Xantrex XDC 300-20 Digital DC Power Supply. The applied voltages ranged from 12.5 to 100 V (equivalent to 31.25–250 V·cm⁻¹). The deposition time was 1 min in all cases. The current was measured by a voltage drop over a resistance of 10 kΩ.

Samples were characterized by the current plots measured during EPD, mass difference before and after EPD (Mettler AT261 Delta Range®), SEM micrographs (Hitachi S-4800), white light profilometer (Cotec Altisurf) and contact angle measurements.

2.3. Sintering

The temperature range of burning out of the polystyrene beads was preliminarily determined by TG-DTA (Thermo Gravimetric-Differential Thermal Analysis). The TG-DTA was performed on a dried drop of suspension in oxygen atmosphere at 5 °C/min.

Sintering was carried out up to a maximal temperature of 900 °C hold for 2 h, with a heating rate of 300 °C/min/h and a cooling rate of 160 °C/min/h, in inert atmosphere (argon purity 99.9999%, flow rate 3 l/min). In order to allow for combustion of the PS beads, the furnace was aerated for 2–3 min when the heating temperature reached the burning temperature of PS determined by TG-DTA.

3. Results

The procedure of particle functionalization of Fig. 1 allowed for the preparation of TiO₂-PS composite particles suspended in isopropanol,

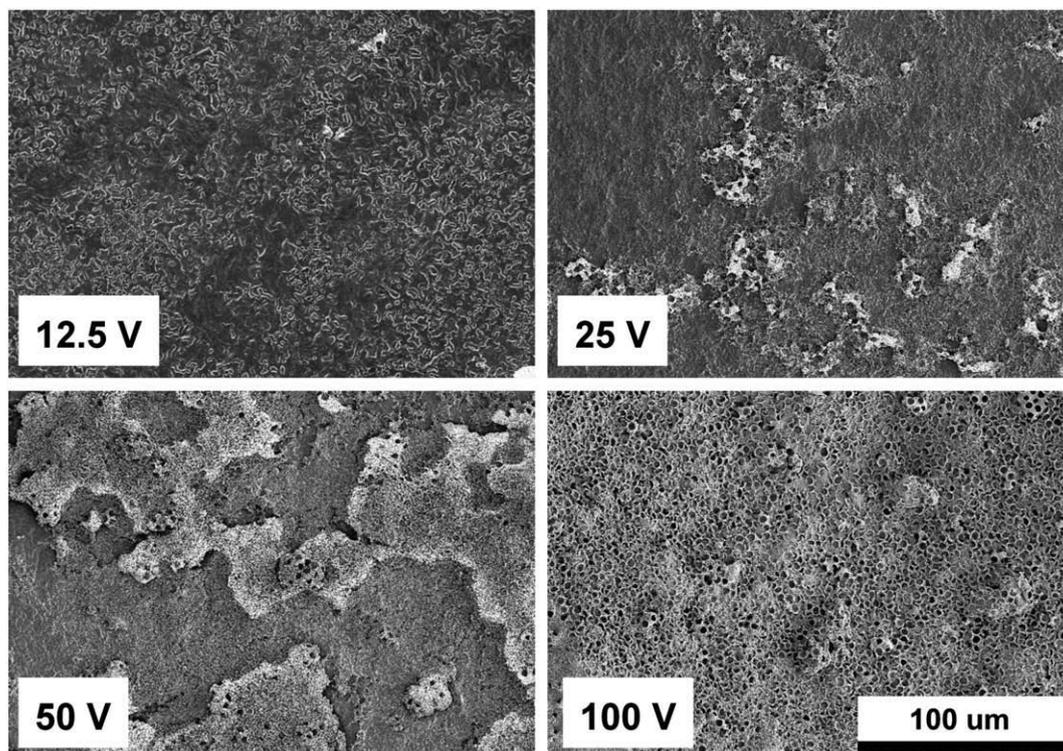


Fig. 6. Secondary electron SEM micrographs of TiO₂-PS coatings obtained at 12.5, 25, 50 and 100 V EPD (1 min) after sintering (argon flow, maximal temperature of 900 °C hold for 2 h, aeration for 2–3 min at 260–270 °C).

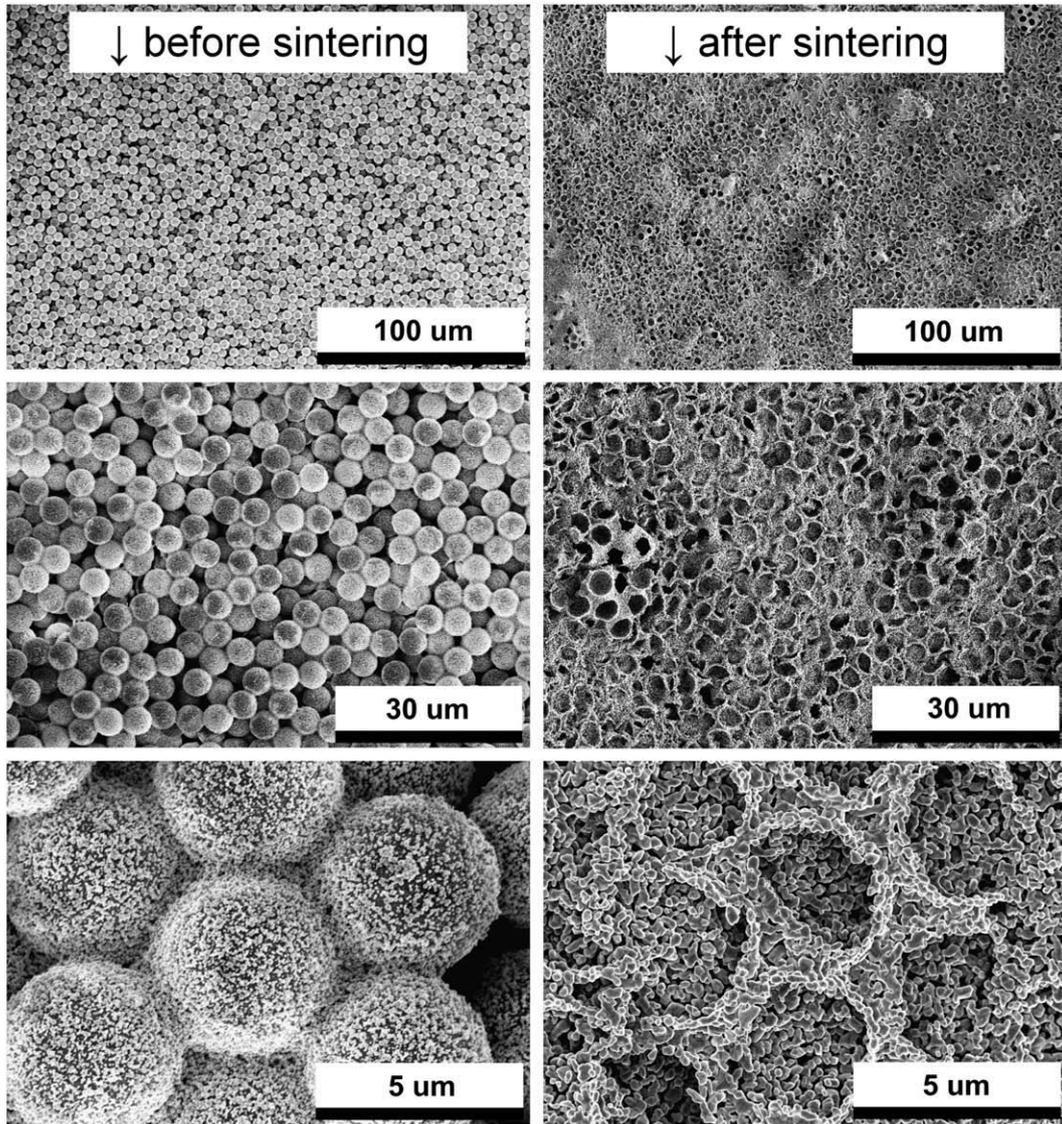


Fig. 7. Secondary electron SEM micrographs at different magnifications of TiO_2 -PS coatings obtained at 100 V EPD (1 min) before sintering (on the left) and after sintering (on the right).

with no excess of TiO_2 submicron particles. Fig. 3 reports a SEM micrograph of the composite particles from a dried drop of suspension. The suspension stability resulted high enough in relation to the time frame of the EPD experiments (1 min): a sedimentation line in the 12 ml centrifuge tube started to be visible only after 20 min.

A full coating could be obtained independently of the applied voltage only with the particle concentration of ≈ 8 vol.% TiO_2 -PS (obtained from 7.2 vol.% PS and 0.43 vol.% TiO_2 suspensions). Two EPD tests were carried out for each applied voltage using the ≈ 8 vol.% TiO_2 -PS isopropanol suspension. The corresponding current curves and deposited mass values are shown in Fig. 4. Average thickness of the coatings estimated by white light profilometry resulted in: 22 μm for the 12.5 V EPD; 26 μm for the 25 V EPD; 100 μm for the 50 V EPD and 130 μm for the 100 V EPD.

According to the TG-DT analysis on a sample of PS beads the mass loss given by PS burning out started at ca. 260 $^\circ\text{C}$ and ended up at ca. 405 $^\circ\text{C}$ (see Fig. 5). Based on this result, the furnace was aerated for 2–3 min in the temperature range of 260–270 $^\circ\text{C}$ (the argon flow was interrupted during this time). SEM observation of the samples after sintering (900 $^\circ\text{C}$, 2 h) revealed that only the coatings deposited at 100 V were characterized by a multi-scaled surface given by the burnt PS microbeads and the sintered TiO_2 submicron particles. Sintering of

the samples from EPD at the voltages from 12.5 V to 50 V caused a collapse of the whole coating (case of 12.5 V) or part of it (case of 25 V and 50 V), with no controlled multi-scaled surface left. This is clearly illustrated in the SEM micrographs of Figs. 6 and 7.

Contact angle values were calculated from measurements on digital pictures of microliter water droplets on the sintered coatings obtained with the different voltages (12.5 V–100 V). The results are given in Table 1. For comparison: two droplets on the Ti6Al4V bare surface of 2 samples outside the coated area showed contact angles of 60.0 $^\circ$ and 65.6 $^\circ$. The decrease of contact angle measured on the sample with multi-scale structured surface (EPD 100 V) in comparison to the other cases with measured angles around 60 $^\circ$ is shown in Fig. 8.

Table 1

Contact angle values calculated from measurements on digital pictures of microliter water droplets on the sintered coatings obtained with different voltages (12.5 V–100 V).

Sample from EPD voltage	Contact angle
12.5 V	66.0 $^\circ$
50 V	59.8 $^\circ$
100 V	36.2 $^\circ$

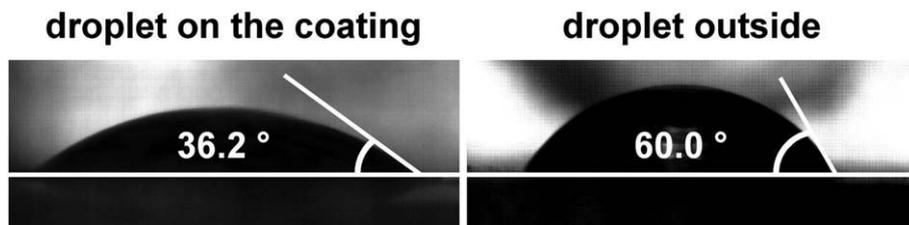


Fig. 8. Digital images of microliter water droplets used to measure the contact angle on the sintered coating with multi-scale structured surface obtained after EPD under 100 V (on the left). For comparison, a droplet on the bare substrate is shown (on the right).

4. Discussion

In the particle functionalization process, the initial steps of PS dilution, NH_3 and PDADMAC addition in the flow diagram of Fig. 1 were discussed in our previous publication [12]. Compared to the procedure previously published, new centrifugation steps with intermediate redispersion of the sediment in water and acid aqueous solution before final centrifugation and redispersion in isopropanol were introduced. In addition, the use of a doubled particle concentration was adopted (final PS concentration 7.6 vol.% instead of 3.8 vol.%). These changes in the particle functionalization process were found to substantially increase the suspension stability and to enhance the EPD performance. This was confirmed by a reduced sedimentation rate and a more efficient EPD process. In fact, coatings up to 130 μm could be deposited at 100 V for 1 min, in contraposition to the 10–15 μm thick coatings deposited at 300 V for 10 min of our previous work [12]. Finally, thanks to the enhanced EPD performance the removal of the sample from suspension after EPD occurred without evidence of coating drop down.

The gradual change of suspension medium from alkaline to neutral to acid before final redispersion in isopropanol reinforced the charge inversion of the already formed TiO_2 -PS composite particles. In fact, the surface charge of the composite particles was given by the TiO_2 submicron particles covering the PS beads. The isoelectric point of TiO_2 is at pH 5–6. For this reason, composite particles were negatively charged in the alkaline medium used for heterocoagulation between functionalized PS and TiO_2 particles. On the other hand, cathodic EPD required positively charged particles. Intermediate centrifugation steps with redispersion in an aqueous acid solution were meant to increase the positive charge of the TiO_2 outer submicron particles before dispersion in isopropanol (the TiO_2 submicron particles used in this study gain a positive charge when dispersed in isopropanol) [12]. The final centrifugation step with careful redispersion of the sediment in isopropanol was found to be crucial in order to keep the ionic strength of the suspension low. Ions deriving from the previous acid medium could be reduced avoiding charge screening and a decreased EPD efficiency (particles and not free ions are meant to be the main charge carriers).

The thickness of the deposited TiO_2 -PS composite particles was found out to be a critical parameter for the coating morphology after sintering. The desired multi-scale structured surface was achieved only after sintering of the thicker deposit obtained in this study (130 μm corresponding to ca. 25 layers of particles after EPD 100 V). In fact, sintering with burning out of the PS beads generally caused a collapse of the entire coating. The outer coating surface maintained a multi-scale topography only if the collapsed TiO_2 coating did not condense incorporating the surface particle layers in it. The transition in sintering behaviour from full to partial condensed coating with conservation of the multi-scale surface topography can be clearly seen in the micrographs of Fig. 6. A parametric study with different coating thickness and variable sintering conditions would be required in order to better understand this phenomenon and to more finely tailor the sintered coating morphology. Additionally, in order to assess an application of these coatings in the bone-implant fixation

interface of orthopaedic implants, mechanical characterization of the coatings with particular attention to shear stress resistance would be mandatory.

The change of contact angle observed on the sintered coatings obtained from different coating thickness represents an interesting finding in the fields of biomedical implants and biosensors. The 3-steps procedure generating multi-scale structured surfaces presented here can be considered as a potential new technique to prepare surfaces with wettability gradients. For example, the thickness of the deposits along one preferential direction of one sample can be varied using electrodes with variable interdistance (Hull Cell). Based on the results presented in this work, sintering of TiO_2 -PS coatings with a gradient in thickness is expected to be characterized by a gradient in wettability. In fact, an emerging effort to prepare surface-chemical and -morphological gradients (determining wettability) used to investigate protein adsorption and cell adhesion behaviours has been recently documented in a review paper [17].

5. Conclusions

The method for the preparation of TiO_2 -PS composite particles in organic suspensions presented in a previous publication was further investigated. Centrifugation and redispersion steps in specific media were introduced. In addition, particle concentration was increased. In this way, a controlled EPD of TiO_2 -PS particle was achieved using relatively low voltage and deposition times. The deposited TiO_2 -PS particle layers were sintered at 900 $^\circ\text{C}$ for 2 h in an argon flow with a short aeration time for the combustion of the PS beads. The sintering treatment caused collapse and densification of the TiO_2 matrix. In the thicker coatings (<100 μm), a multi-scale structured surface with relatively high wettability was originated from the burning out of the PS microsized beads and the sintering of the submicron TiO_2 particles.

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