



# Formation of mixed and patterned self-assembled films of alkylphosphonates on commercially pure titanium surfaces



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## ABSTRACT

Titanium is extensively employed in biomedical devices, in particular as implant. The self-assembly of alkylphosphonates on titanium surfaces enable the specific adsorption of biomolecules to adapt the implant response against external stimuli. In this work, chemically-tailored cpTi surfaces were prepared by self-assembly of alkylphosphonate molecules. By bringing together attributes of two grafting molecules, aqueous mixtures of two alkylphosphonates were used to obtain mixed self-assembled films. Single self-assembled films were also altered by laser abrasion to produce chemically patterned cpTi surfaces. Both mixed and patterned self-assembled films were confirmed by AFM, ESEM and X-ray photoelectron spectroscopy. Water contact angle measurements also revealed the composition of the self-assembly films. Chemical functionalization with two grafting phosphonate molecules and laser surface engineering may be combined to guide the bone-like formation on cpTi, and the future biological response in the host.

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## 1. Introduction

Titanium is the main metal employed for dental implantology, although there are still various challenges to solve, such as the improved healing response and speed-up of osseointegration [1]. Rapid growth of osseous tissue on the implant is unusually observed. Biomaterials for dental implantology must be still improved to reduce the loading time and to promote the osseointegration in difficult sites with low quality or amount of bone [2]. Bone-like apatite formed on titanium may serve as scaffold for natural bone tissues.

Surface properties of implants are identified as crucial to achieve osseointegration because the surface rules most biological events [3]. Bone tissue growth on an implant surface may be stimulated by varying its surface characteristics [4–6], including the chemical modification with self-assembly techniques [7,8]. Modification of commercially pure Titanium (cpTi) [9–12] with Self-Assembled

*Abbreviations:* ODP, Octadecylphosphonic acid; UDP, 11-Hydroxyundecylphosphonic acid; PDDPA, 12-phosphonododecylphosphonic acid; PHDA, 16-phosphonohexadecanoic acid; cpTi, Commercially pure titanium; DLP, Direct Laser Patterning; SAF, Self-assembled film; THF, Tetrahydrofuran; SBF, Simulated body fluid.

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Films (SAF) of phosphonates provides chemical stability and surface specificity to the implant [13–18]. The properties of cpTi surfaces might be modulated by chemically heterogeneous or patterned SAFs. This would enable to guide the bioadhesive response. It is interesting to examine if surface heterogeneities induced on cpTi may accelerate or mitigate the bone-like apatite growth.

Phosphonates have been demonstrated to form SAFs on titanium oxide substrates as a result of their high affinity towards the metal oxide surfaces, with surface hydroxyl groups [13,14]. Tosatti et al. prepared mixed self-assembled monolayers from aqueous mixtures of two organophosphates amphiphiles molecules [19]. Morgenthaler et al. employed organophosphate molecules to obtain chemical gradients [20]. Laser ablation is an effective method for patterning surfaces with different purposes [21–26]. Direct Laser Patterning (DLP) provides better control of the microscale texture on the implant surface. Laser-treated cpTi surfaces offer great possibilities in dental implantology. Clinical studies point out to enhanced bone formation on the laser treated area of implant [27,28]. Fernández-Rodríguez et al. utilized DLP for selective desorption of alkylphosphonates adsorbed on smooth cpTi surfaces [29]. Tizazu et al. employed interferometric lithography on titanium oxide surfaces, previously modified with alkylphosphonate SAMs, to produce nanopatterns [30].

In this work, two routes were followed to modify cpTi surfaces based on mixed and patterned SAFs of organophosphonates.

We employed DLP for the preparation of chemically-patterned cpTi surfaces from single SAFs of two different organophosphonates (carboxyl- and methyl-terminated surfaces). Mixed SAFs were formed by using different aqueous mixtures of hydroxyl- and phosphonate-terminated organophosphonates. We characterized the physico-chemical features of the two types of chemically-tailored cpTi surfaces.

## 2. Experimental

### 2.1. Materials

Titanium samples were prepared from cpTi [31] ingots of ASTM grade II (Manfredi). The ingots were cut into discs with an initial height of 1.6 cm and 1.6 cm in diameter. Since molecular films adsorbed on rough titanium surfaces present usually lower order than those ones formed on smooth surfaces [32], we polished the cpTi discs with a grinder (Beta Grinder Polisher, Buehler) until we reached nanometric-scale roughness ( $R_q \geq 0.4$  nm and  $R_a \geq 0.6$  nm, measured with an atomic force microscope over an area of  $1 \mu\text{m}^2$ ).

Four organophosphonate molecules were used in this work: 11-hydroxyundecylphosphonic acid (UDPA, (-OH) terminal group, Sigma Aldrich), 12-phosphonododecylphosphonic acid (PDDPA, (-PO(OH)<sub>2</sub>) terminal group, Sigma Aldrich), 16-phosphonohexadecanoic acid (PHDA, (-COOH) terminal group, Sigma Aldrich) and octadecylphosphonic acid (ODPA, (-CH<sub>3</sub>) terminal group, Sigma Aldrich). Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), tetrahydrofuran (THF), acetone and ethanol were grade reagents provided by Sigma Aldrich. All the chemical products and solvents were used as received without additional purification, and Milli-Q water was used for the preparation of aqueous suspensions and soaking.

### 2.2. Titanium discs preparation

The cpTi surfaces were cleaned to remove residual glue and polishing agents by ultrasonic baths in acetone, soapy water, ethanol and Milli-Q water. Then, the cpTi surfaces were dried with nitrogen. The clean cpTi samples were stored in Petri dishes to avoid eventual pollution. To reduce the native oxide layer and organic residues of the cpTi surfaces, a radio frequency plasma device (KX1050 Plasma Asher, Emitech) with argon gas was employed. The samples were treated for 15 min at 25 W with a flow rate of 15 ml/min. Next, the cpTi samples were immersed in Milli-Q water for 24 h to enhance and stabilize the oxidation state of titanium. Afterwards, the samples were placed in an oven during 15 min at 140 °C to dehydrate the cpTi surfaces just before the SAF formation [33].

### 2.3. Mixed self-assembled films

We prepared five 1 mM aqueous mixtures of UDPA and PDDPA with different UDPA fractions (0,  $\frac{1}{4}$ ,  $\frac{1}{2}$ ,  $\frac{3}{4}$ , 1). To dissolve completely the two molecules in water, the solution was heated up to 50 °C and stirred simultaneously. Clean and hydroxylated cpTi discs were immersed (10 ml/disc) for 5 days in each mixture in the dark. Then, the samples were placed in an oven during 1 h at 140 °C to enhance the covalent bond of the SAF to the cpTi surface. The organophosphonate excess on the surface was removed in an ultrasonic bath of K<sub>2</sub>CO<sub>3</sub> at 0.5 M (2:1 ethanol:water) for 5 min, and next in an ultrasonic bath of Milli-Q water for 10 min. Finally, the samples were dried under nitrogen flow.

### 2.4. Patterned self-assembled films

We prepared two 1 mM solutions of PHDA and ODPA in THF. Dehydrated cpTi surfaces were immersed (10 ml/disc) for 5 days

in each solution of organophosphonate. It should be emphasized that the use of a nonpolar solvent enables the self-assembly of alkylphosphonates on hydrophilic surfaces. As the hydrophilic phosphonate head intends to avoid the nonpolar solution, it is oriented towards the solution-air interface and on the hydrophilic oxide surface. This facilitates a priori well-compacted and ordered alkylphosphonate film on the native titanium oxide surface [34]. Once the surface functionalization was initiated, the procedure followed was identical to the mixed SAFs.

The cpTi surfaces modified separately with single SAFs of ODPA and PHDA were ablated with a Nd:YAG 532 nm laser (E-20 SHG II, Rofin) with a pulse width of 1  $\mu\text{s}$ . The laser beam intensity and ablation direction were optimized to desorb selectively the single SAF with minor damage of the underlying cpTi surface.

Two types of ablation templates were reproduced in this work: striped patterns ( $8 \times 12 \text{mm}^2$ ) centred on each SAF with different nominal widths, varying from 5 to 100  $\mu\text{m}$  (See Fig. 1 a-b), and a half of each SAF (half of a disc with dimensions of  $16 \times 8 \text{mm}^2$ ) was uniformly ablated (Fig. 1c). The stripe-to-stripe distance was selected to be equal to the stripe width. Laser ablation was performed twice with  $I = 13.5$  A and 13.8 A, respectively. The second laser ablation was performed at 90° respect to the first pass. The beam speed ( $v = 25$  mm/s), frequency of pulse ( $f = 15$  kHz) and laser spot width (1  $\mu\text{m}$ ) were fixed during all laser irradiations.

### 2.5. Characterization of self-assembled films

#### 2.5.1. Atomic Force Microscopy (AFM)

Height and phase images of the SAFs were acquired using a MultiMode Scanning Probe Microscope (Nanoscope IV, Veeco) in tapping mode. The phase images allowed detecting the presence of heterogeneous surface domains in the SAF.

#### 2.5.2. Environmental scanning electron microscope (ESEM)

High resolution backscattered electron images were obtained with an ESEM (FEI, Quanta 400) to examine the patterned SAFs without high vacuum

#### 2.5.3. X-ray photoelectron spectroscopy (XPS)

The surface chemistry of the SAFs was quantified by XPS with an Axis Ultra-DLD (Kratos) with a maximum depth resolution of 10 nm. XPS measurements were performed at a take-off angle of 45° with respect to the sample surface. The data measured were analysed with CasaXPS (Casa Software Ltd), which enabled to examine the oxygen and carbon signals.

#### 2.5.4. Contact angle measurement

The wettability of the SAFs was evaluated with the tilted plate method. The instrument employed is described by Montes Ruiz-Cabello et al. [35]. Milli-Q water was used in all experiments. Contact angle measurements were performed at room temperature and by triplicate. The drop volume was 40  $\mu\text{l}$  to assure the sliding down of drop.

## 3. Results and discussion

### 3.1. Topography study

Fig. 2 presents the AFM topographies of the mixed SAFs. The roughness parameters of the mixed SAFs are collected in Table 1. The images reveal disordered structures with spots and clusters but there is no correlation with the molar fraction used in the aqueous mixture. The explanations for the disorder in the SAF structures are various. There are up to five possible binding ways for the phosphonate adsorption on the titanium oxide surface [36]. The difference between them is marked by the number of oxygen atoms attached

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