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Electrochemical co-deposition of phosphonate-modified carbon nanotubes and tantalum on Nitinol

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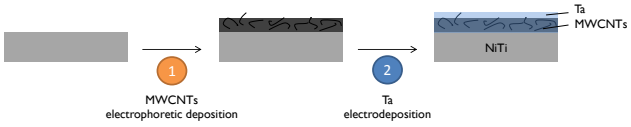
Nitinol substrates are coated with thin surface films made of carbon nanotubes (CNTs) and tantalum (Ta), in the perspective of fostering their osseointegrative aptitudes. Exceptional mechanical and chemical characteristics of nanotubes combined with capacity of resistance to corrosion and strong bioactive properties of tantalum allow for the generation of adherent, protective and functional layers on metallic biomaterial platforms. The composite coatings are elaborated on Nitinol through a two-step electrochemical protocol, firstly with electrophoretic deposition (EPD) of phosphonate-modified CNTs, secondly with electrodeposition (EDP) of Ta. As a preliminary step, phosphonate groups, acting further as specific tantalum capture entities, are introduced on the nanotubes sidewalls by means of diazonium derivatives, which imply no hard oxidative treatment. X-ray photoelectron spectroscopy (XPS), scanning (SEM) and transmission (TEM) electronic microscopies are used to analyse the chemical composition, structure and morphology of the different layers.

Introduction

Composite layers made of metals/ceramics and nanoparticles constitute recent promising developments in numerous nanomaterials and surface treatments topics. Application fields stretch from automobile industry to medical devices, aeronautics, electronics, sensors, energy storage, and many others. Main processing techniques consist of powder metallurgy, thermal spraying, sol-gel, or electrochemistry.[1-4]

This paper specifically features tantalum (Ta) and carbon nanotubes (CNTs) as components of hybrid thin films deposited on titanium-based substrates via electrochemical process. The aim of the present study fits into the design of robust, functional and biocompatible platform biomaterials for orthopaedic applications such as prosthesis and medical equipment. Concretely, the base substrate is Nitinol (NiTi) – an almost equiatomic nickel-titanium alloy –, exploited here for its good criteria of biocompatibility and resistance to corrosion. Its mechanical characteristics of shape-memory, superelasticity and high-damping capacity are particularly sought in the elaboration of flexible articular implants. However, specific strategies are required to reduce the immune response due to the possible release of nickel-containing species in the human body, which can provoke allergenic and carcinogen effects over time, but also to consolidate the barrier effect towards aggressive agents from the external environment.[5-8] With this perspective, a thin Ta coating will be deposited on the NiTi surface in order to increase chemical stability and protection towards corrosion, as well as to reinforce abilities of osseointegration and radio-opacity.[9-11] In addition, the remarkable properties of multiwalled carbon nanotubes (MWCNTs) allow for their use as filling elements within a composite layer. Indeed, they have been proved to boost the (bio)chemical reactivity through the introduction of selected functional groups on the tubes sidewalls, to mechanically strengthen the surface layer, and to bring biomimetic elements with the collagen fibre structure.[1-3,12]

The simultaneous electrochemical deposition of two constituents is somehow regarded as more complex than that of single one. Several experimental parameters from the solvent (polarity, electrochemical window, viscosity …) and/or the nanoparticles (nature, size, concentration, dispersion ability ...) must be carefully and synergistically pondered: their residual impacts on surface morphology, mechanical resistance and chemical composition of the deposits are often of crucial importance.[4,13-16] For these reasons, we consider hereafter a two-step experimental protocol (Scheme 1). First an electrophoretic deposition (EPD) of chemically-modified MWCNTs on NiTi plates is performed: this fast and cost-effective technique involves simple equipment and is applicable to a large variety of materials.[16-19] This phase is followed by the electrodeposition (EDP) of Ta on the MWCNTs/NiTi substrates in an ionic liquid solution, a method selected here for its practical easiness and its high capacity of controlling the morphology, thickness and composition of the deposited material.[20,21] It is also expected that the metallic coating electrodeposited on the nanotubes surface achieves strong bonding between MWCNTs and Ta.



Scheme 1. Preparation of 1) MWCNTs/NiTi samples through MWCNTs electrophoretic deposition (EPD), and 2) Ta/MWCNTs/NiTi samples through Ta electrodeposition (EDP).

The present study involves the use of chemically-modified MWCNTs. Such treatments are required for allowing the homogeneous and stable dispersion of the nanotubes in the

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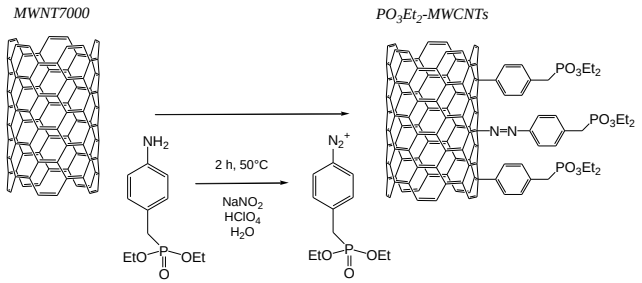
solvent used for their EPD on NiTi.[22-24] These functionalizations can also be considered as a direct way to introduce on the nanotubes sidewalls chemical functions presenting a strong affinity for tantalum entities during their EDP on MWCNTs/NiTi. Functional groups considered here consist of phosphonate ($–PO_3R_2$) derivatives, given the high affinity of phosphonic acids for Ta.[25,26] Several reports have already described the covalent grafting of $–PO_3R_2$ groups at the surface of CNTs:[27-30] among these, our recent paper has highlighted the direct binding of bisphosphonic acid functions on MWCNTs, with the introduction of two $–PO_3H_2$ moieties per anchoring point, and the formation of strong covalent P–C–P bonds directly on the outer surface of the nanotubes.[30] However, the synthesis protocol of such bisphosphonic-modified nanotubes resorts to oxidized carbon MWCNTs. Classically, such oxidative modifications result in shortened nanotubes with lower aspect ratios which can involve a partial loss of their mechanical resistance capacities, in particular when they are eventually included into composite coatings.[31] Therefore, we envisage here another well-known method of MWCNTs functionalization, clean and less aggressive (implying no oxidative treatments), through the covalent grafting on CNTs sidewalls of diazonium salts species,[32-34] bearing in this case $–PO_3Et_2$ terminal functions (Scheme 2).



Scheme 2. Functionalization protocol of phosphonate-modified MWCNTs.

Elaboration of composite layers on titanium-based substrates for orthopedic biomaterials perspectives is thus described and commented hereafter. A two-step electrochemical process is considered, first with EPD of diethyl phosphonate-modified MWCNTs (PO_3Et_2-MWCNTs) on NiTi plates, then with Ta EDP on PO_3Et_2-MWCNTs/NiTi surfaces. Both processes constitute choice techniques of high precision for producing thin coatings from liquid solutions. The different layers and their components are characterized by X-ray photoelectron spectroscopy (XPS), scanning (SEM) and transmission (TEM) electronic microscopies.

Results and Discussion

The initial stage of this study is devoted to the setting up of experimental parameters for the EPD of PO_3Et_2-MWCNTs on NiTi in aqueous solution. After preliminary trials (unshown results), a potential difference of 25 V and a deposition time of 1 min have been determined as optimal values for obtaining thin uniform and adherent layers. Following the deposition procedure, a thermal post-treatment of the samples at 120°C during 5 h is performed to reinforce the films compaction and toughness.

PO_3Et_2-MWCNTs are first characterized through XPS analyses in order to validate the presence of the phosphonate functions on the nanotubes sidewalls. The representative survey spectrum of the CNTs powder presented on Figure 1a exhibits an intense C1s peak, characteristic of carbon nanotubes and carbon atoms of the benzylphosphonate terminal functions. PO_3Et_2 groups are also identified through P2p and O1s signals at respective binding energies (E_b) of 133.5 and 532.5 eV. The probable occurrence of diazo links (Scheme 2), unreacted diazonium salt and/or residual aniline precursor is assessed by the N1s contribution at 400.4 eV.[33] Similar observations in terms of peaks existence and position are made for electrophoretically-deposited PO_3Et_2-MWCNTs on NiTi (Figure 1b), confirming their presence on the metallic substrates.

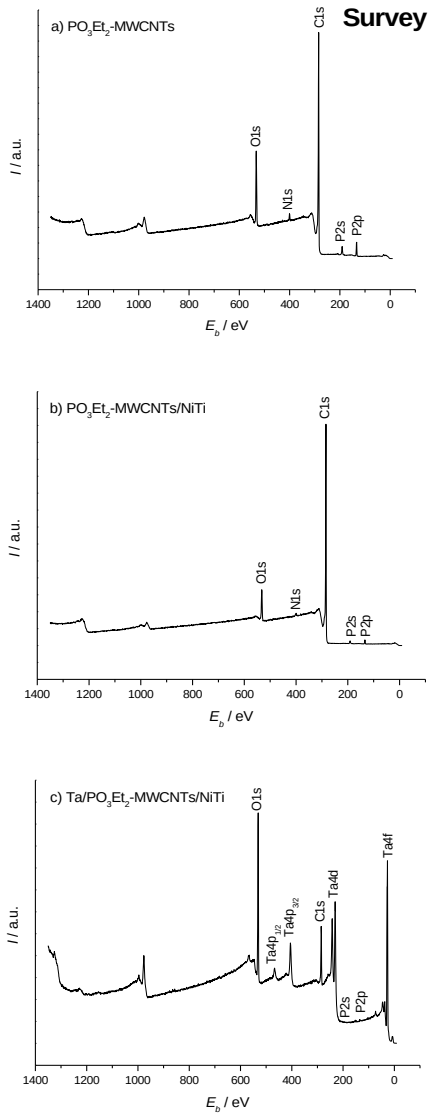


Figure 1. XPS survey spectra of a) PO_3Et_2-MWCNTs, b) PO_3Et_2-MWCNTs/NiTi, and c) Ta/PO_3Et_2-MWCNTs/NiTi samples (with a Ta EDP time of 60 min).

Global atomic percentages for both samples are presented in Table 1. Very interestingly, P(2p), N(1s) and O(1s) quantities slightly decrease from the MWCNTs powder to the EPD sample. It should indicate that MWCNTs bearing quantitatively less PO_3Et_2 functions have been preferentially deposited on the NiTi surfaces.

Table 1. Global XPS atomic percentages.

Substrate	C1s [%]	O1s [%]	P2p [%]	N1s [%]	Ta4f [%]	F1s [%]
PO_3Et_2-MWCNTs	80.7	14.1	3.4	1.8	//	//
PO_3Et_2-MWCNTs/NiTi	88.0	8.6	1.8	1.6	//	//
Ta/PO_3Et_2-MWCNTs/NiTi[a]	40.0	44.6	1.2	//	13.5	0.7

[a] With a Ta EDP time of 60 min.

This trend is confirmed by the further analysis of the C1s core level for both substrates. Figure 2 shows the corresponding spectra. Seven entries are identified: carbide-like species (traces) at 282.0 eV (1), C=C from MWCNTs and satellite "shake-up" peak at 284.1 eV (2) and 290.4 eV (7), C-C and C-H at 285.0 eV (3), C-N, C-O and C-P=O at 286.0 eV (4), C-P-O at 286.9 eV (5), and oxidized contaminations (classically C(=O)O at 288.5 eV (6).[33,35-37] Table 2 details the atomic percentages of the different contributions. As observed with global atomic percentages (Table 1), contributions typical of PO_3Et_2-modified nanotubes (3 to 5) are reduced after the EPD step. In parallel, percentages of the "crude" nanotubes contributions (2 and 7) increase, which witnesses the residual presence of less PO_3Et_2-modified MWCNTs in the layer within substantial proportions.

Table 2. XPS atomic percentages of the different contributions in the C1s core level signal.

Substrate	Components [%]						
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
PO_3Et_2-MWCNTs	0.6	66.2	15.0	8.9	5.0	2.6	1.7
PO_3Et_2-MWCNTs/NiTi	0.9	76.2	10.3	5.6	3.0	2.0	2.0
Ta/PO_3Et_2-MWCNTs/NiTi[a]	2.0	38.9	31.5	15.3	7.6	2.7	2.0

(1) Carbide. (2) C=C_{MWCNTs}. (3) C-C,C-H. (4) C-N,C-O,C-P=O. (5) C=O,C-P-O. (6) C(=O)O. (7) Shake-up or CO_3^{2-}.
[a] With a Ta EDP time of 60 min.

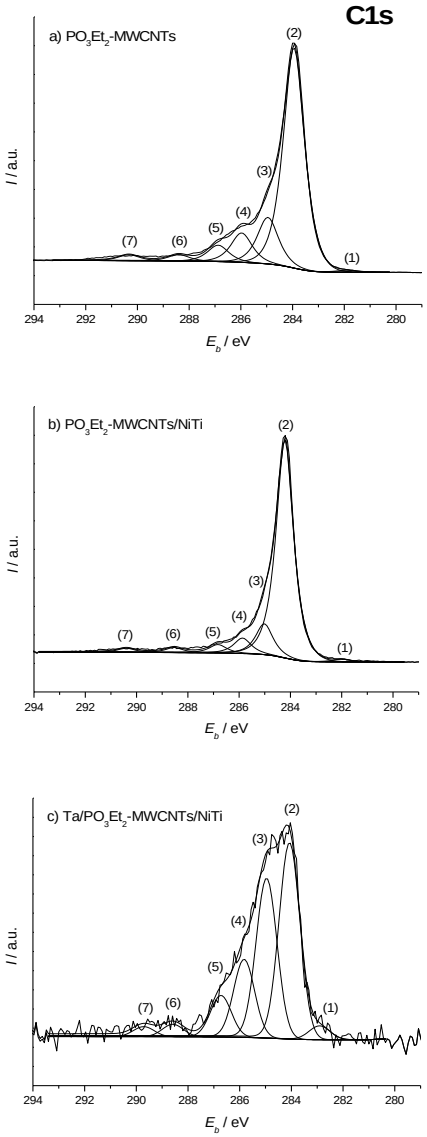


Figure 2. XPS C1s core level of a) PO_3Et_2-MWCNTs, b) PO_3Et_2-MWCNTs/NiTi, and c) Ta/PO_3Et_2-MWCNTs/NiTi samples (with a Ta EDP time of 60 min).

For the further Ta EDP on the PO_3Et_2-MWCNTs/NiTi surfaces, explorative experiments are first undertaken in order to determine optimized practical conditions of deposition method and time. As noticed in previous studies,[38,39] the galvanostatic deposition process leads to better results in terms of Ta adherence compared to cyclic voltammetry or potentiostatic mode. A current density value of -100 µA/cm², determined as optimal for the EDP of Ta on Ti and NiTi surfaces,[38,39] is used again here. A comparative study involving SEM and XPS measurements is then conducted to describe the evolution of the Ta EDP process over time. Morphological features of the Ta/PO_3Et_2-MWCNTs/NiTi samples are analyzed by SEM for 1, 30, 60 and 120 min durations and compared with unchanged PO_3Et_2-MWCNTs/NiTi counterparts (Figure 3a). The punctual apparition of the first nanometric Ta particles on the nanotubes is already noticed after 1 min (red circles on Figure 3b). Wrapping by Ta progressively increase after 30 min (Figure 3c),

with a granular but more uniform structure. A 60 min deposition time leads to thicker and smoother Ta layers around CNTs (Figure 3d). Ultimately, the 120 min treatment (Figure 3e) brings no more significant morphological change, with a global aspect obviously similar to the previous case.

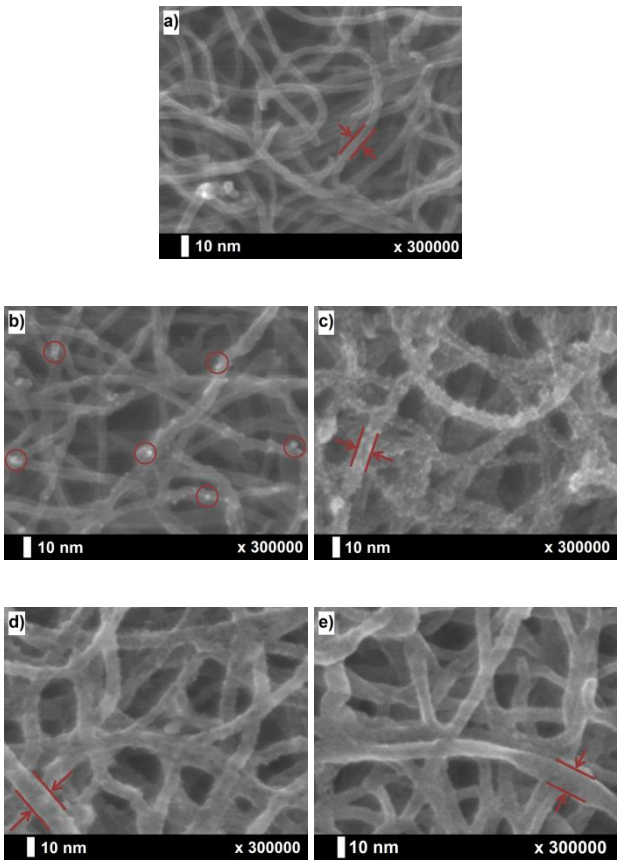


Figure 3. SEM pictures of a) PO_3Et_2-MWCNTs/NiTi and Ta/PO_3Et_2-MWCNTs/NiTi samples after a Ta electrodeposition time of b) 1 min, c) 30 min, d) 60 min, and e) 120 min.

Thickness values of the Ta film on the CNTs are estimated from SEM images of uncoated (Figure 3a) and coated (Figure 3b-e) nanotubes (red delimitations) and reported in Table 3. If the sporadic Ta deposits obtained after 1 min cannot be considered as a real wrapping of the CNTs (quasi-zero experimental value), average measurements obtained for longer durations are more consistent, raising from 3.5 nm after 30 min to 5.0 nm after 60 min, and 6.0 nm after 120 min. XPS Ta/C=C_{MWCNTs} experimental ratios (Table 3) further explain the increase of Ta quantity deposited on the nanotubes with time, from 0.02 after 1 min to 0.12 after 30 min, 0.85 after 60 min and 1.07 after 120 min. In parallel, Ta/F ratios rise progressively up to 60 min (21.07) and then decrease abruptly after 120 min (6.7). This seems to be indicative of an overload behavior occurring for long EDP times (larger than 60 min), with a residual sorption of more TaF_x (with $x \leq 5$) contaminant species on the substrates. Such achievements, leading to F-enriched Ta layers, have thus to be avoided for biocompatibility reasons.[40]

Table 3. Ta_2O_5 wrapping, and XPS Ta/F and Ta/C=C_{MWCNTs} ratios of the different Ta/PO_3Et_2-MWCNTs/NiTi substrates.

EDP time	Wrapping [nm]	Ta/C=C_{MWCNTs}	Ta/F
1 min	~0	0.02	2.0
30 min	3.5	0.12	4.3
60 min	5.0	0.85	21.2
120 min	6.0	1.07	6.7

The 60 min Ta EDP case can thus be endorsed as an optimum in terms of layer adherence, structure, thickness, and fewness of fluorine contaminants. Detailed XPS characterizations are described on Figures 1c (survey spectrum) and 2c (C1s core level), and on Tables 1 (global atomic composition) and 2 (contributions for C1s signal). In addition to residual C1s, O1s and P2p signals testifying for the presence of the PO_3Et_2-MWCNTs, characteristics peaks of the Ta deposit (Ta4f) and slight F contaminations (F1s) from the LiF additive are observed. The increase of aliphatic carbon proportions at 285.0 eV (3), as well those of C-N and C-O at 285.8 eV (4), C=O at 286.7 eV (5), C(=O)O at 288.6 eV (6) and CO_3^{2-} at 289.7 eV (7),[35,36] is attributed to further contamination inherent to the EDP process. Tantalum is detected in its oxidized form Ta_2O_5 at 26.6 eV ($Ta4f_{7/2}$ signal). The experimental O/Ta ratio is 3.3, the theoretical value for Ta_2O_5 being 2.5. The slight oxygen excess is thus attributed to the oxygen atoms of the PO_3Et_2 groups on the MWCNTs, and to inherent atmospheric contamination.

Pristine and Ta-covered PO_3Et_2-MWCNTs/NiTi substrates are also compared through SEM at different magnifications (Figure 4). The nanotubes covering by $Ta(_2O_5)$ is clearly observed.

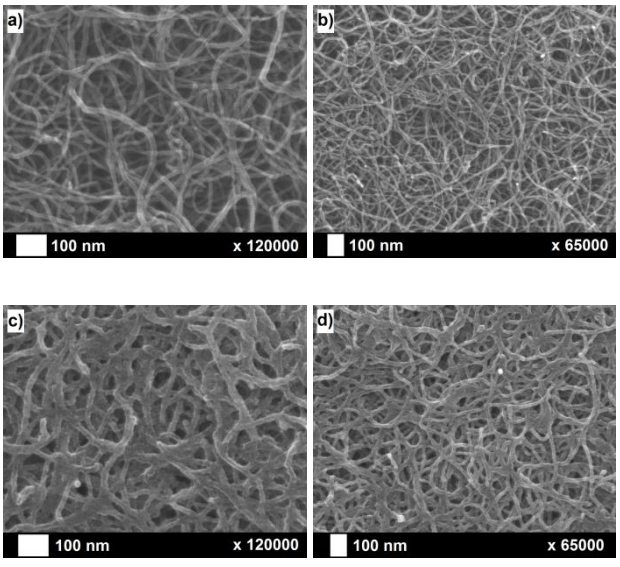


Figure 4. SEM pictures of a,b) PO_3Et_2-MWCNTs/NiTi and c,d) Ta/PO_3Et_2-MWCNTs/NiTi samples (with a Ta EDP time of 60 min).

In order to perform TEM analyses of the Ta/PO_3Et_2-MWCNTs composite itself, the layers are scratched from the NiTi substrates and carefully dispersed in absolute ethanol, then a drop of the suspension is deposited on a TEM grid for characterization.[30] Corresponding image (Figure 5) shows the strongly adherent and compact nature of Ta on the nanotubes.

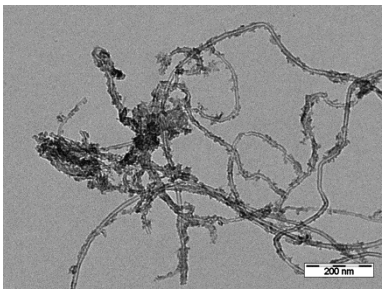


Figure 5. TEM picture of the Ta/PO_3Et_2-MWCNTs composite (with a Ta EDP time of 60 min) scratched from the NiTi surface.

Conclusions

The combination of phosphonate-modified MWCNTs EPD and Ta EDP processes has led to adherent, tough and homogeneous composite layers on NiTi plates. Carbon nanotubes appear as compactly and regularly deposited on the metallic surfaces. Their further modification by tantalum leads to strong and uniform Ta_2O_5-wrapping coatings of ~ 5 nm thickness. Such hybrid surface films are thus strongly believed to constitute choice platforms for further osseointegrative purposes. The occurrence of well-dispersed and uniformly-Ta-covered carbon nanotubes at the direct interface between the NiTi biomaterial and the human body can significantly improve mechanical and chemical interactions between the elements, and generate preferential sites for bone cells adhesion and proliferation.

Additional experimental analyses and studies are expected to complete and corroborate the first results presented here. Electrochemical characterisations at global (polarization curves, impedance measurements) and local (scanning electrochemical microscopy) scales would bring useful and explicit data in connection with corrosion protection issues. Extensive examinations of the mechanical features (stress testing) and bioactive aptitudes (hydroxyapatite growth, osteoblasts/osteoclasts colonisation) of the tantalum/carbon nanotubes composites would also assume a particular importance for specific applied perspectives.

More generally, concepts and methodologies presented in this work can be extended to other application fields such as sensors, electrodes, batteries, and flame-retardant (nano)materials.

Experimental Section

Synthesis of PO_3Et_2-MWCNTs: 0.240 g of MWNT 7000 carbon nanotubes (Nanocyl) are mixed with 2.004 g of diethyl 4-aminobenzylphosphonate (ABCR, 99%) and 0.552 g of sodium nitrite ($NaNO_2$, Sigma-Aldrich, ≥99.0%) in 120 mL of ultra-pure water (18.2 MΩ cm). 828 µL of perchloric acid ($HClO_4$, Acros, 70%) are then added to the solution, which is stirred at 50°C for 2 h (Scheme 2). The samples are finally filtered and washed with distilled water, then dried for storage and further use.

NiTi substrates preparation: NiTi rectangular plates (20 mm x 10 mm x 0.3 mm) are purchased from AMF and constituted of Ni (56%) and Ti (balance). They are first mechanically polished on a Buehler EcoMet 300/AutoMet 250 instrument using silicon carbide papers (P800, then P1200) and diamond pastes (9, 3, then 1 µm) from Struers. NiTi coupons are then cleaned in absolute ethanol (VWR Prolabo) under ultrasonication for 15 min, submitted to UV-ozone for 30 min (Jelight 42-220), and finally ultrasonically rinsed in absolute ethanol for 15 other min, before being blown dry under nitrogen.

EPD of PO_3Et_2-MWCNTs on NiTi: 2.5 mg of PO_3Et_2-MWCNTs are dispersed into 15 mL of ultra-pure water using a Hielscher UP200S Ultrasonic Processor, and the resulting suspension is centrifuged in a Thermo Scientific Jouan B4i instrument for 30 min at 3000 rpm. 10 mL of the supernatant are then withdrawn as working solution for the EPD experiments. These are carried out with a pre-treated NiTi plate as anode and a platinum foil as cathode. The two electrodes are placed parallel to each other, separated by 5 mm, and present an area of contact with the CNTs dispersion of 1 cm². A constant potential difference of 25 V is applied for 1 min using a Voltcraft VLP-2403 Pro DC power supply, to allow the migration of the nanotubes towards the NiTi surface. The PO_3Et_2-MWCNTs/NiTi substrates are then carefully removed from the solution, and finally dried in an oven at 120°C for 5 h.

EDP of Ta on PO_3Et_2-MWCNTs/NiTi: The covering of PO_3Et_2-MWCNTs/NiTi substrates by an electrodeposited Ta coating is realized in an argon-filled glove box (residual quantities of water and oxygen below 30 ppm), using an EG&G Princeton Applied Research, Potentiostat/Galvanostat Model 263A. The working bath contains 0.10 M tantalum fluoride (TaF_5, Aldrich, 98%) and 0.25 M lithium fluoride (LiF, Sigma-Aldrich, ≥99%) in dry 1-butyl-1-methyl bis(trifluoromethylsulfonyl)imide ionic liquid ([BMP]Tf_2N, IoLiTec, 99%). Ta EDP is processed under galvanostatic mode at ambient temperature (25°C): a constant current density of -100 µA/cm² is applied during a predefined time to the PO_3Et_2-MWCNTs/NiTi working electrode *versus* a platinum foil acting as both reference and auxiliary electrodes. These are placed parallel to each other at a distance of 2 cm, and immersed in the experimental bath to have a 1 cm² surface in contact with the solution. The modified samples are further post-treated by careful rinsing with acetone (Chem-Lab, 99+%), immersed for 15 min in boiling water, rinsed with absolute ethanol, and blown dry under nitrogen.

XPS characterization: XPS spectra are measured on a Thermo Scientific K-Alpha spectrometer and treated by means of the Thermo Avantage v5.27 software. The photoelectrons are excited with a monochromatic Al Kα radiation as the excitation source, collected perpendicularly to the sample surface and detected with a hemispherical analyser. The spot size of the XPS source is 200 µm, and the analyser is operated with a pass energy of 150 eV for survey spectra and 20 eV for accumulation spectra on core levels. Pressure is maintained below 1 x 10^{-8} Torr during data collection. The binding energies of the obtained peaks are referenced to the C1s for sp3 carbon, set at 285.0 eV. Spectra are fitted with a Smart background and a linear combination of Gaussian and Lorentzian profiles in 70-30 proportions. Peak positions are found essentially constant (± 0.3 eV). The relative peak areas are finally estimated, using following values for sensitivity factors: C1s

1.000, O1s 2.930, P2p 1.192, N1s 1.800, Ta4f 8.620, and F1s 4.430.

SEM and TEM imaging: JEOL 7500F and Phillips Tecnai 10 microscopes are respectively used for obtaining SEM and TEM pictures.

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Keywords: electrochemistry • Nitinol • nanotubes • phosphonate • tantalum

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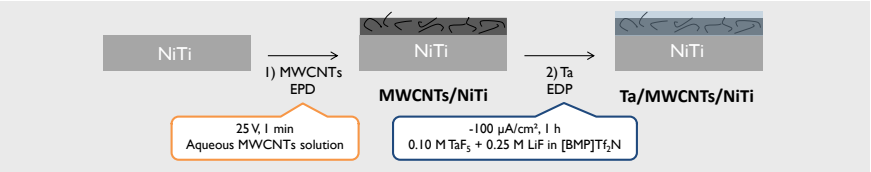

CNTs/Ta composite coatings on NiTi. Carbon nanotubes (CNTs) modified with phosphonate functions are electrophoretically deposited (EPD) on Nitinol (NiTi) plates. They are further coated with a thin tantalum (Ta) electrodeposit (EDP) (see picture). Such adherent and functional surface layers can reinforce mechanical and biochemical interactions with the human body in the framework of osseous implant integration and bone regeneration.

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Electrochemical co-deposition of phosphonate-modified carbon nanotubes and tantalum on Nitinol