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Maho, Anthony; Delhalle, Joseph; Mekhalif, Zineb

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# Electrochemical elaboration and investigation of Nitinol surfaces covered with tantalum, carbon nanotubes and phosphonic acid self-assembled monolayers

Anthony Maho, Joseph Delhalle, and Zineb Mekhalif

Laboratory of Chemistry and Electrochemistry of Surfaces (CES), University of Namur, Belgium  
anthony.maho@unamur.be

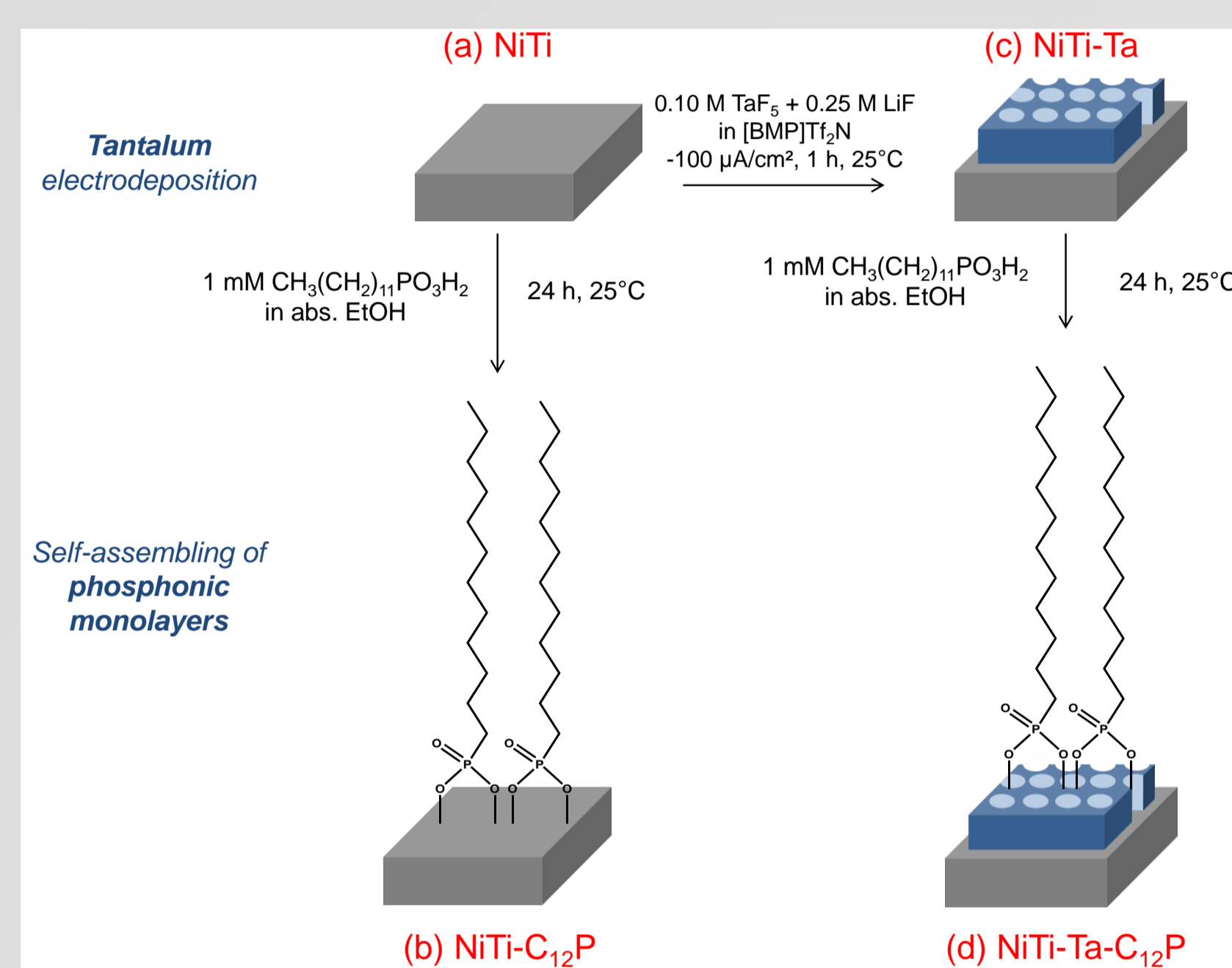
## General context: Ti-based biomaterials

**Titanium and its alloys** constitute very interesting platforms for **dental and osseous biomedical applications** thanks to their low density, high fatigue strength, corrosion resistance, ... More particularly, the **Nitinol** (NiTi) alloy (Ni 56%, Ti balance) is well known for its excellent shape memory and superelasticity properties. However, toxicity of certain alloying elements (Ni in NiTi, Al and V in TiAl6V4 ...), long-term degradation and weak osseointegrative properties remain problematic features.

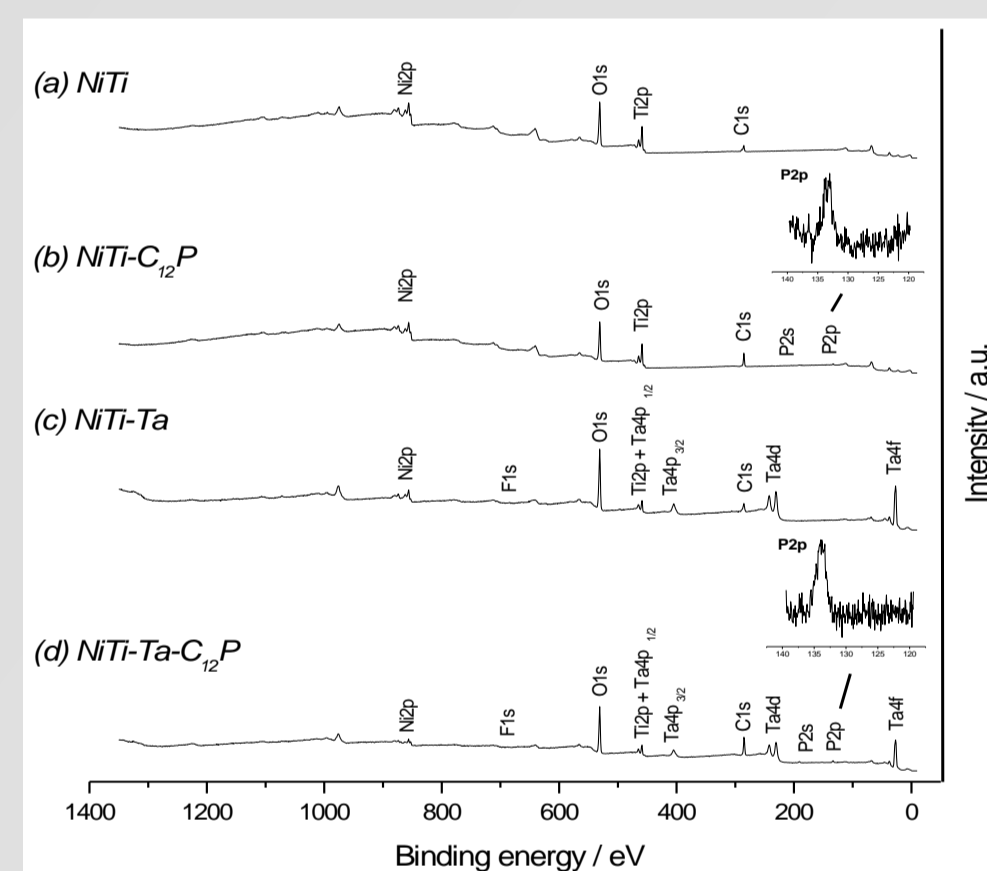
One solving approach stands in the formation of a **thin tantalum coating** on NiTi surface by an **electrodeposition (EDP)** process in **ionic liquids** media: Ta, with its very passivating oxide layer, is highly resistant to corrosion, biocompatible and bioactive, has good radio-opacity ... Additional barrier effect can be brought by the further self-assembly of **alkylphosphonic acid monolayers** [1,2].

Multiwalled **carbon nanotubes (MWCNTs)** can also be incorporated to form a **composite Ta-based coating** on NiTi owing to their ability to improve the mechanical properties of the implant. They can also **specifically interact with osteoblasts and osteoclasts** and promote the bone regeneration process by **mimicking the structure of collagen fibers** and **favor the formation of an hydroxyapatite layer**. Composite Ta-CNTs layers are prepared according a **two-step electrochemical process**, first through the **electrophoretic deposition (EPD)** of **phosphonate-modified MWCNTs** on NiTi, than through the Ta electrodeposition on the NiTi/MWCNTs platforms [3].

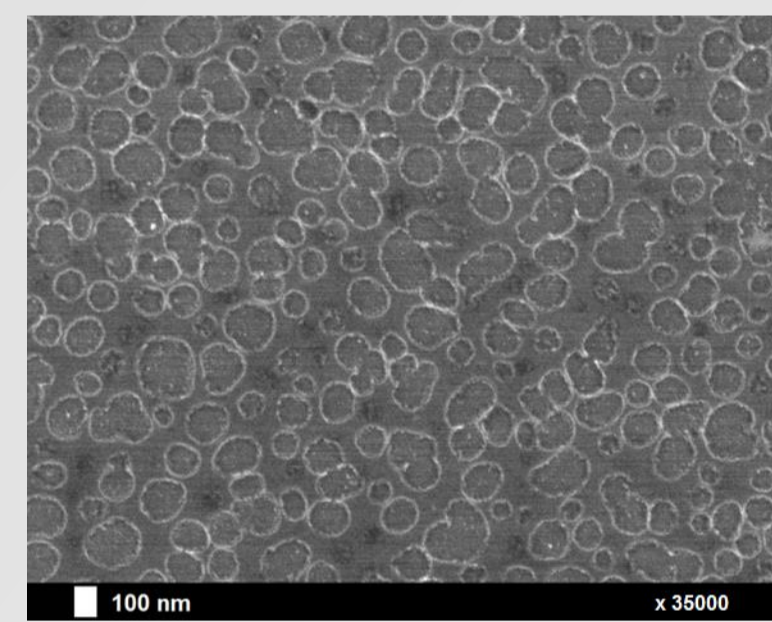
## Ta electrodeposition and alkylphosphonic acids self-assembly on NiTi



XPS – Survey

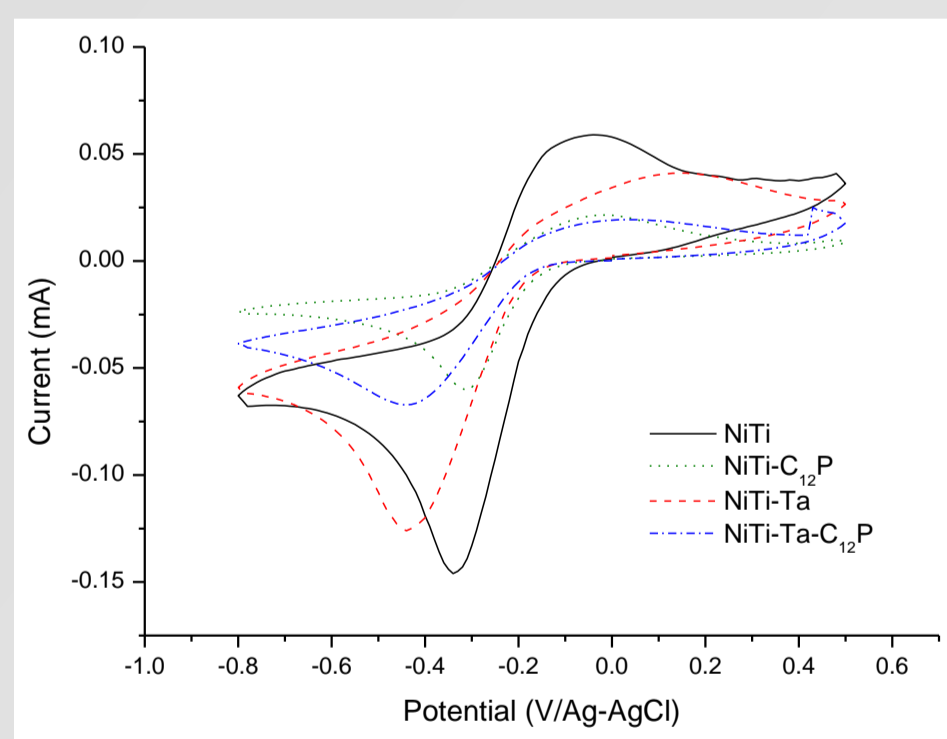


SEM  
NiTi-Ta



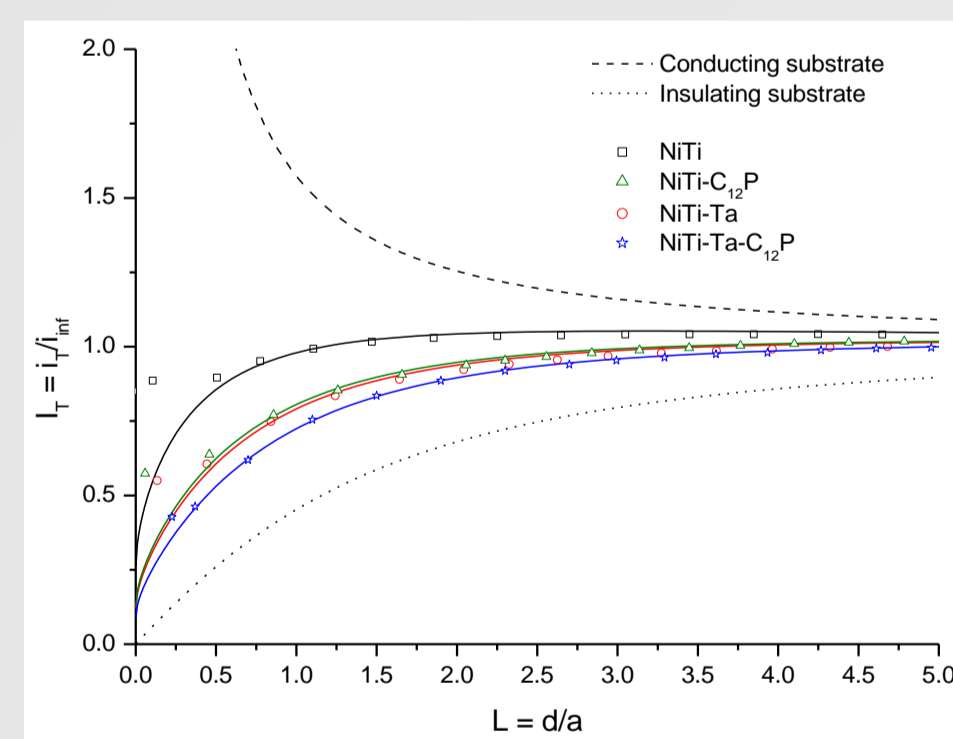
CV

Aqueous 5 mM Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> / 0.1 M K<sub>2</sub>SO<sub>4</sub>  
ν = 20 mV/s



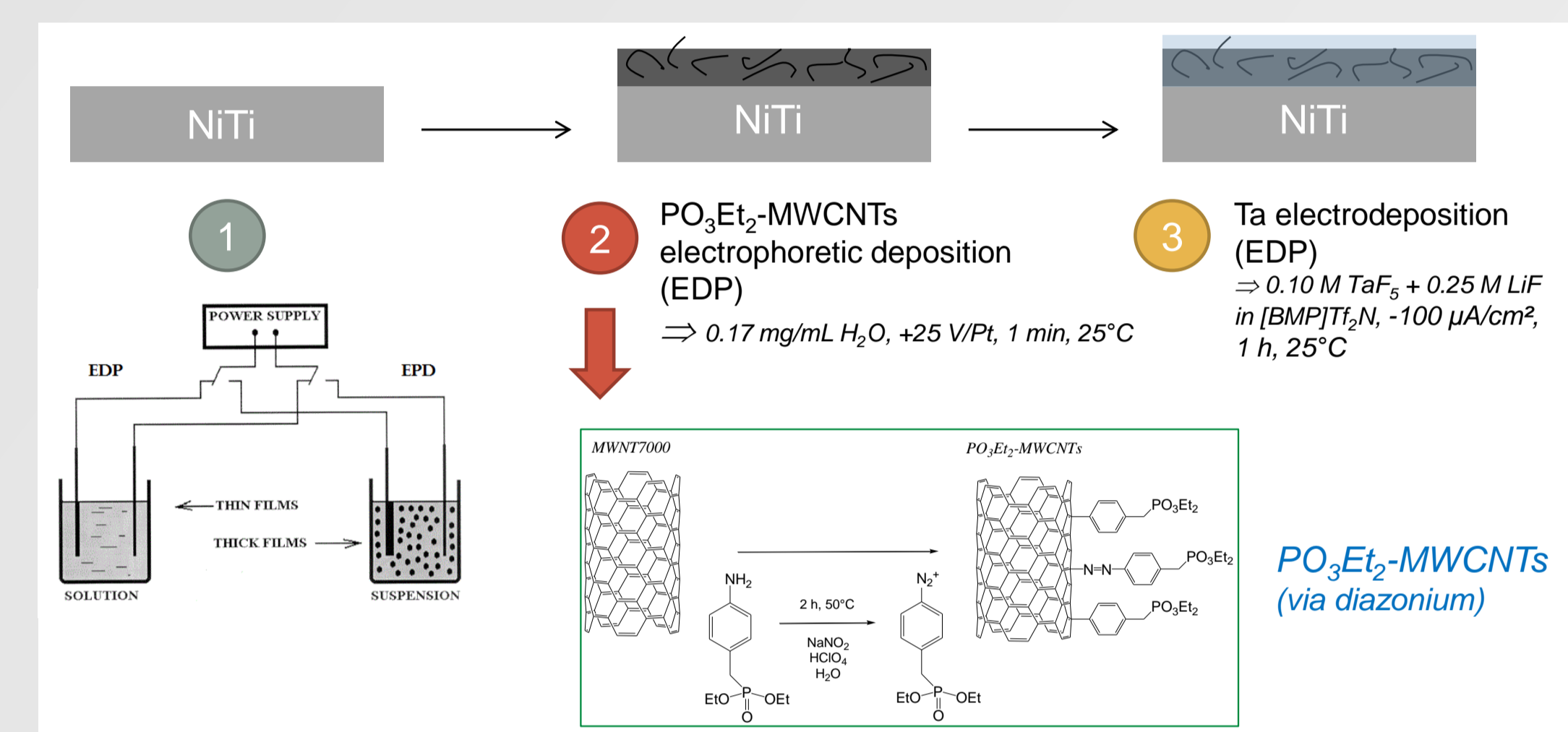
SECM – FB PAC

Aqueous 5 mM Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> / 0.1 M K<sub>2</sub>SO<sub>4</sub>  
E<sub>tip</sub> = -0.70 V/Ag-AgCl; E<sub>substrate</sub> = OCP

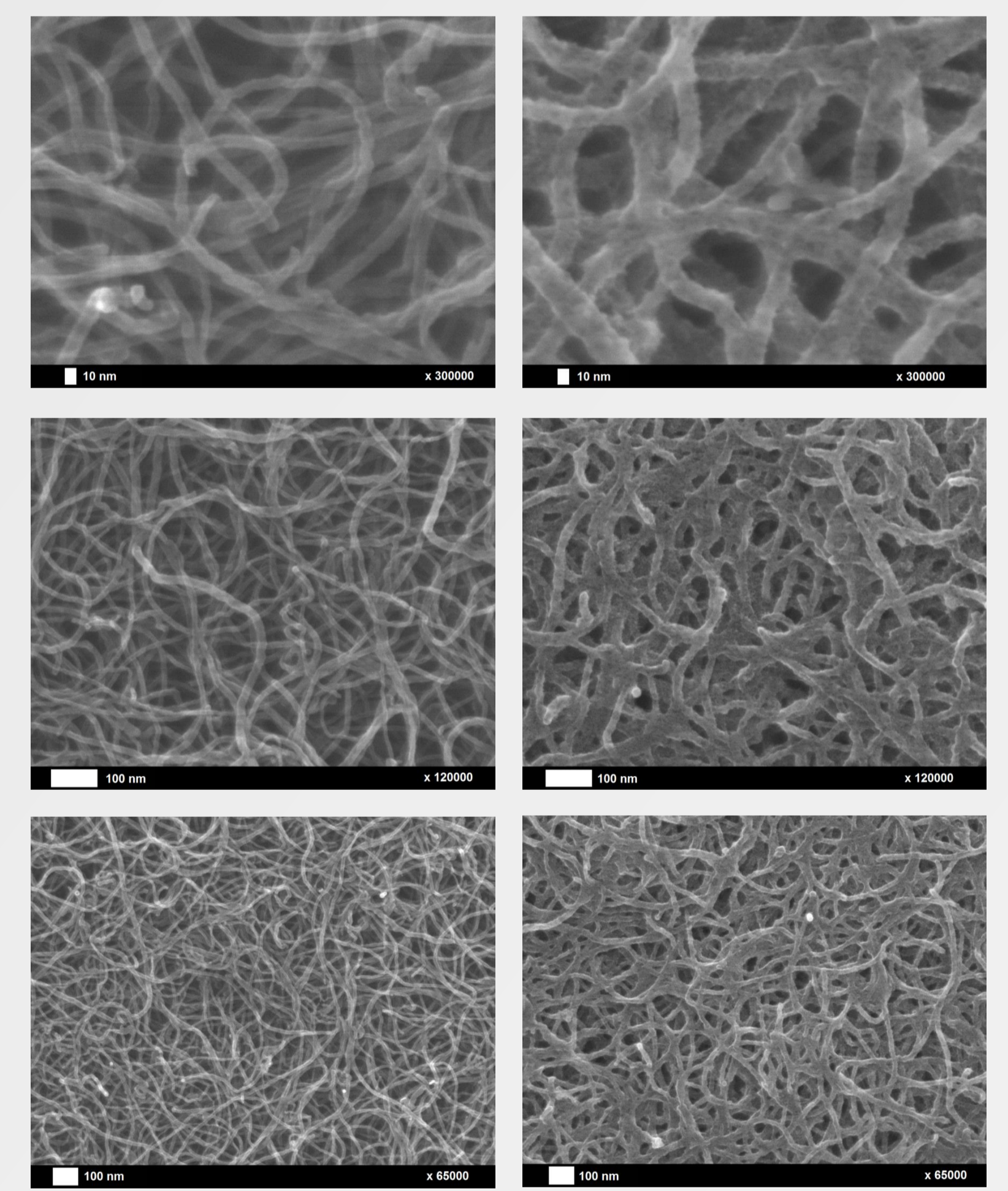


Sample	i <sub>p</sub> (mA)	E <sub>p</sub> (V/Ag-AgCl)	k <sub>app</sub> (10 <sup>-3</sup> cm/s)	k <sub>off</sub> (10 <sup>-3</sup> cm/s)
NiTi	-0.146	-0.34	3.1	4.6
NiTi-C <sub>12</sub> P	-0.060	-0.31	2.9	1.9
NiTi-Ta	-0.126	-0.45	0.92	1.7
NiTi-Ta-C <sub>12</sub> P	-0.067	-0.44	0.87	1.1

## MWCNTs electrophoretic deposition and Ta electrodeposition on NiTi



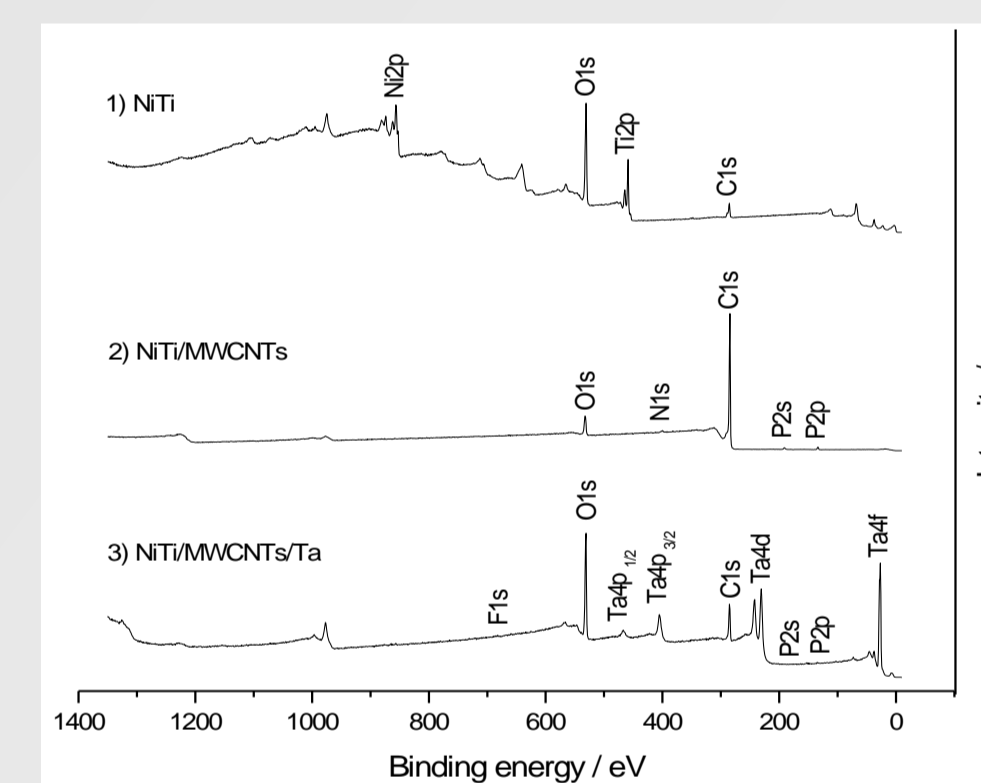
SEM



NiTi/MWCNTs

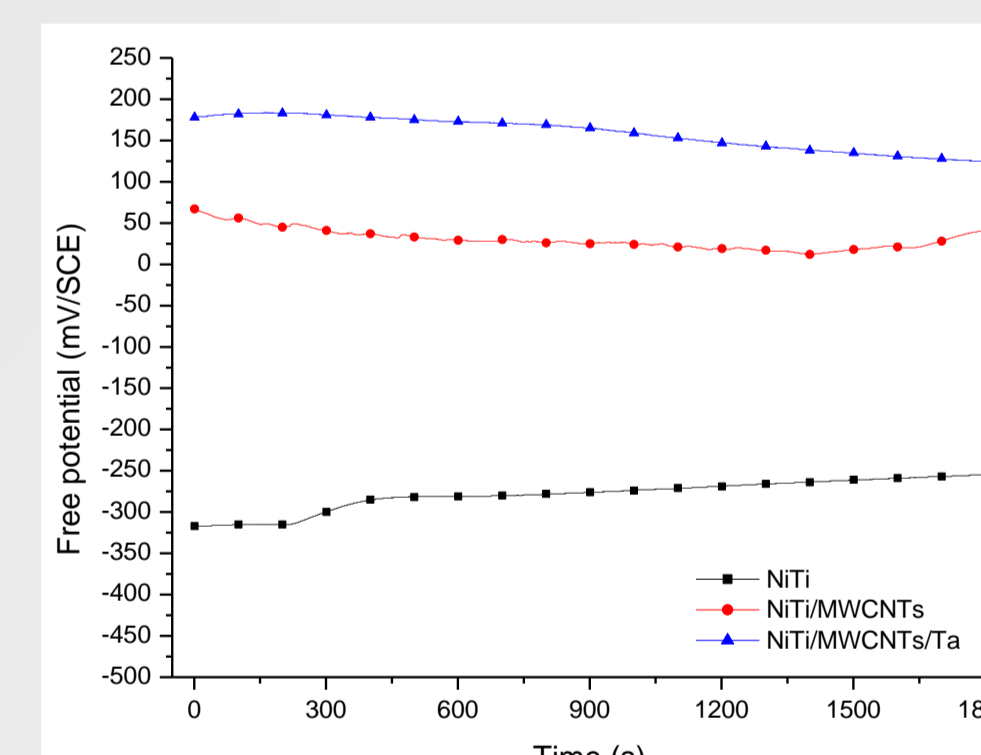
NiTi/MWCNTs/Ta

XPS – Survey



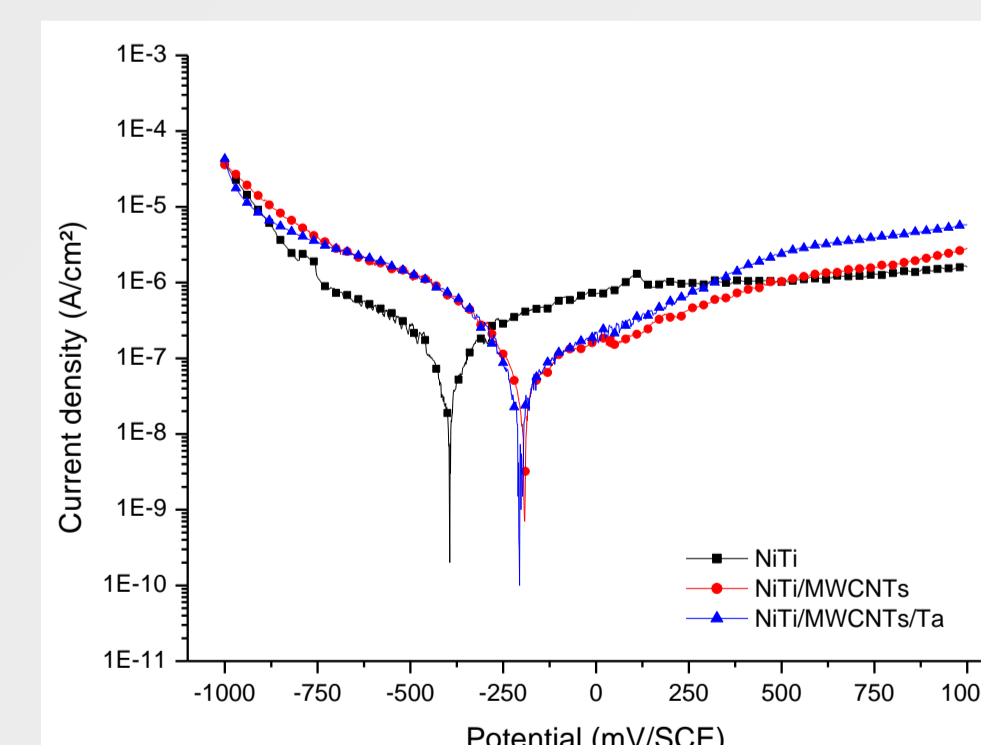
Free potential

Aqueous NaCl 0.9%



LSV

Aqueous NaCl 0.9%  
ν = 1 mV/s



The **electrochemical co-deposition of PO<sub>3</sub>Et<sub>2</sub>-MWCNTs and Ta on NiTi** lead to the generation of **compact, homogeneous and functional composite layers presenting strong barrier properties** at the interface with the external environment.

- **Electrodeposition of a spontaneously nanostructured Ta film** on NiTi (« microscopic » pores; φ ~120 nm).
- **Self-assembly of C<sub>12</sub>P monolayers** on NiTi and NiTi-Ta with surface covering ratios of 68 and 41%, resp. (« macroscopic » defects).  
⇒ Specific electrochemical responses on CV and SECM curves.

## Conclusions and perspectives

- Electrochemistry is used for **both elaboration and characterization of protective and functional surface coatings on Nitinol substrates** with a high level of versatility and precision.
- The considered approaches lead to **highly homogeneous, nanostructured and adherent tantalum-based layers**.
- Such **organic-inorganic hybrid films** are therefore strongly believed to constitute **sensitive platforms for further osseointegrative purposes** (nucleation of hydroxyapatite, adhesion-proliferation of osteoblasts and osteoclasts).

## References

- [1] A. Maho, J. Delhalle, Z. Mekhalif, Study of the formation process and the characteristics of tantalum layers electrodeposited on Nitinol plates in the 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid, *Electrochim. Acta* 89 (2013) 346-358.
- [2] A. Maho, F. Kanoufi, C. Combellas, J. Delhalle, Z. Mekhalif, Electrochemical Investigation of Nitinol/Tantalum Hybrid Surfaces Modified by Alkylphosphonic Self-Assembled Monolayers, *Electrochim. Acta* 116 (2014) 78-88.
- [3] A. Maho, S. Detrich, G. Fonder, J. Delhalle, Z. Mekhalif, Electrochemical Co-Deposition of Phosphonate-Modified Carbon Nanotubes and Tantalum on Nitinol, *ChemElectroChem* (2014) in press.

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