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Elaboration of tantalum oxide and carbon nanotubes composite coatings on titanium for biomaterial applications

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General context: titanium-based biomaterials

- **Titanium and its alloys** constitute very interesting and useful platforms for **dental and osseous biomedical applications** thanks to their low density, high fatigue strength, inertness to human body, corrosion resistance, ... However, toxicity of certain alloying elements (Ni in Nitinol, ...), long-term degradation and weak osseointegration remain problematic features [1].
- One solving approach => formation of a **thin tantalum coating** on Ti surface by **sol-gel** process: Ta, with its very passivating oxide layer, is highly resistant to corrosion, biocompatible and bioactive, has good radio-opacity, ... Nevertheless, high price and important density restrict its use as a bulk material [2].
- Multiwalled **carbon nanotubes (MWCNTs)** can be incorporated to form a **composite Ta-based coating** on Ti 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** [3].
- Hydroxyapatite formation can also be favored by the presence of **molecular films of amino-tris-methylene phosphonic acid** on the Ta₂O₅-based surface. The utilization of such **multifunctional phosphonic acid molecules** is of particular interest, as some -PO₃H₂ functions can be used as strong anchoring feet with the metallic oxide surface while others, acting as terminal groups, directly favor the hydroxyapatite growth at the interface with body environment [4].

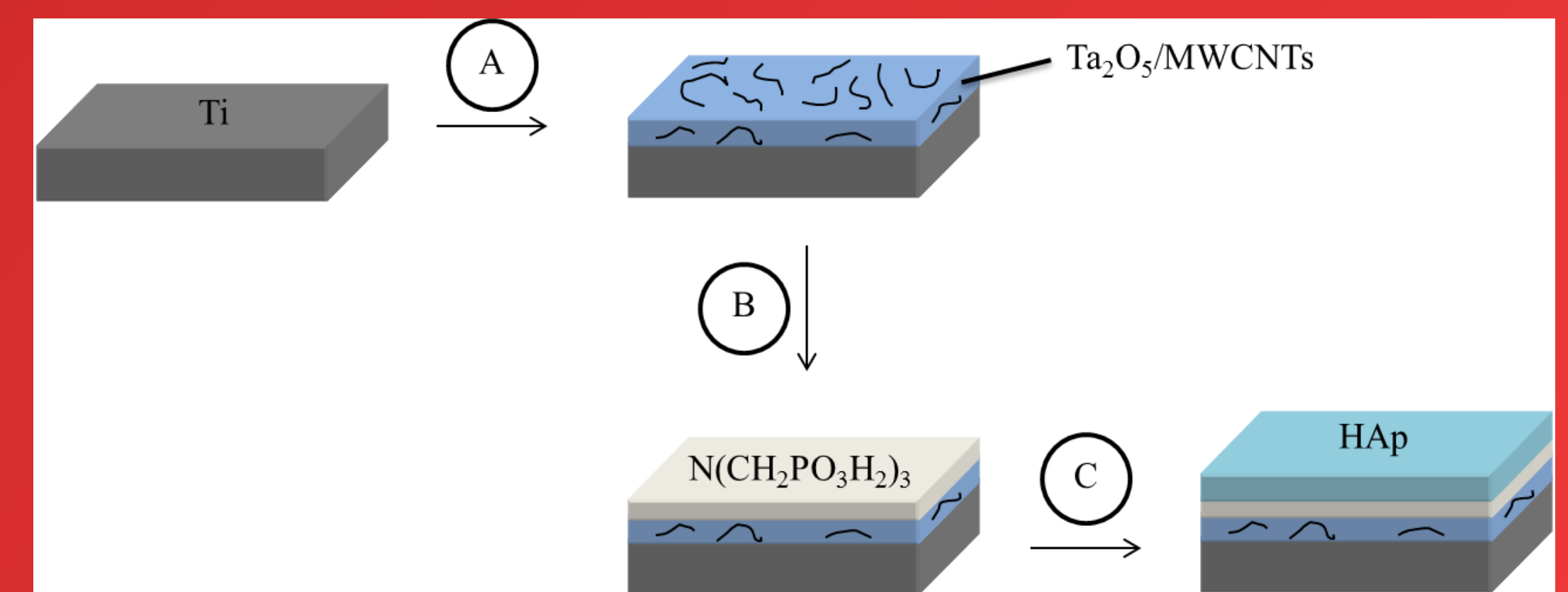
Global strategy

(A) **Sol-gel co-deposition of Ta₂O₅/MWCNTs composite coatings on Ti substrates: optimized treatment**

- ⇒ 10 min immersion in a sol-gel solution made of 4.0 mL abs. EtOH, 0.2 mL of HCl (acid catalyst), and 8.0 mg of oxidized MWCNTs
- ⇒ 10 min gradual hydrolysis in distilled water
- ⇒ 3 min drying at 300°C

(B) **Grafting of an amino-tris-methylene phosphonic acid layer: 1 h immersion in a 10⁻³ M N(CH₂PO₃H₂)₃ aqueous solution at 25°C and pH~1**

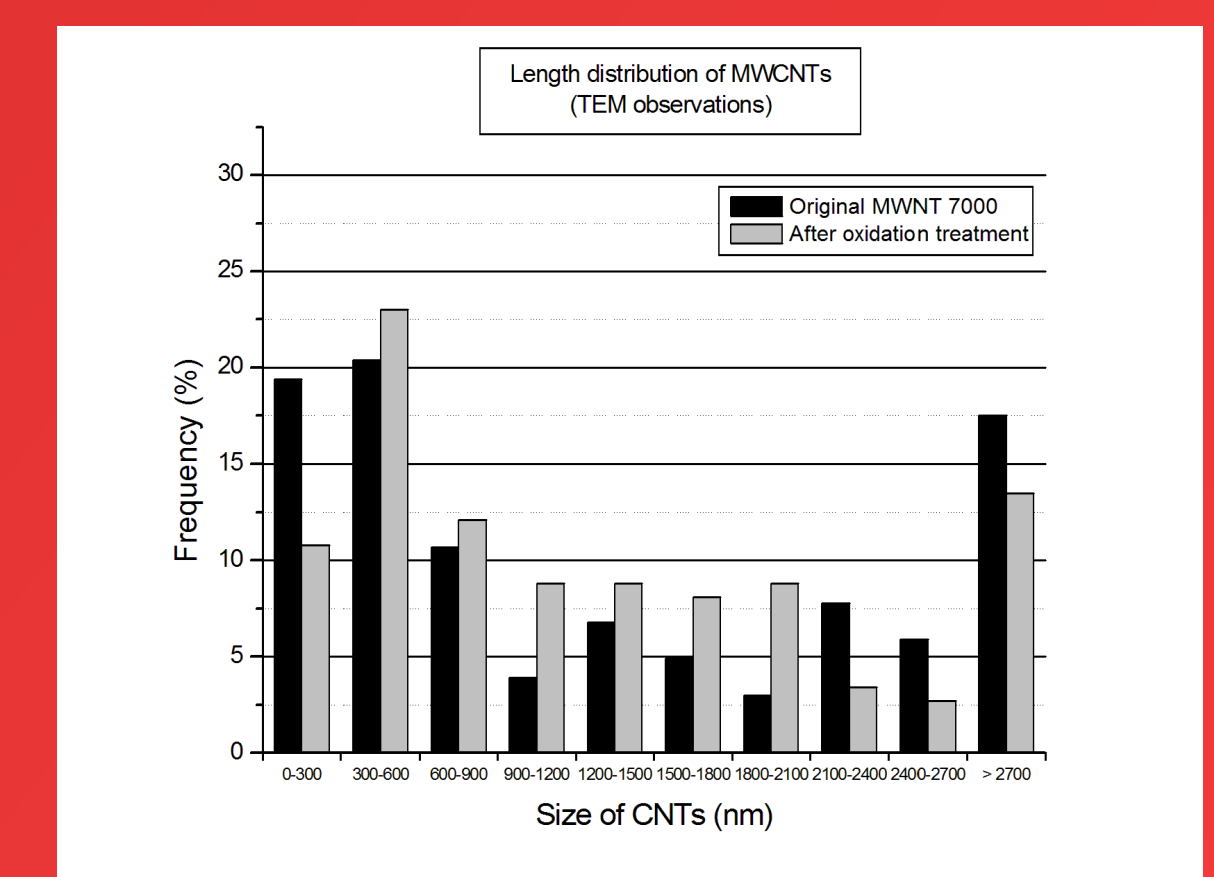
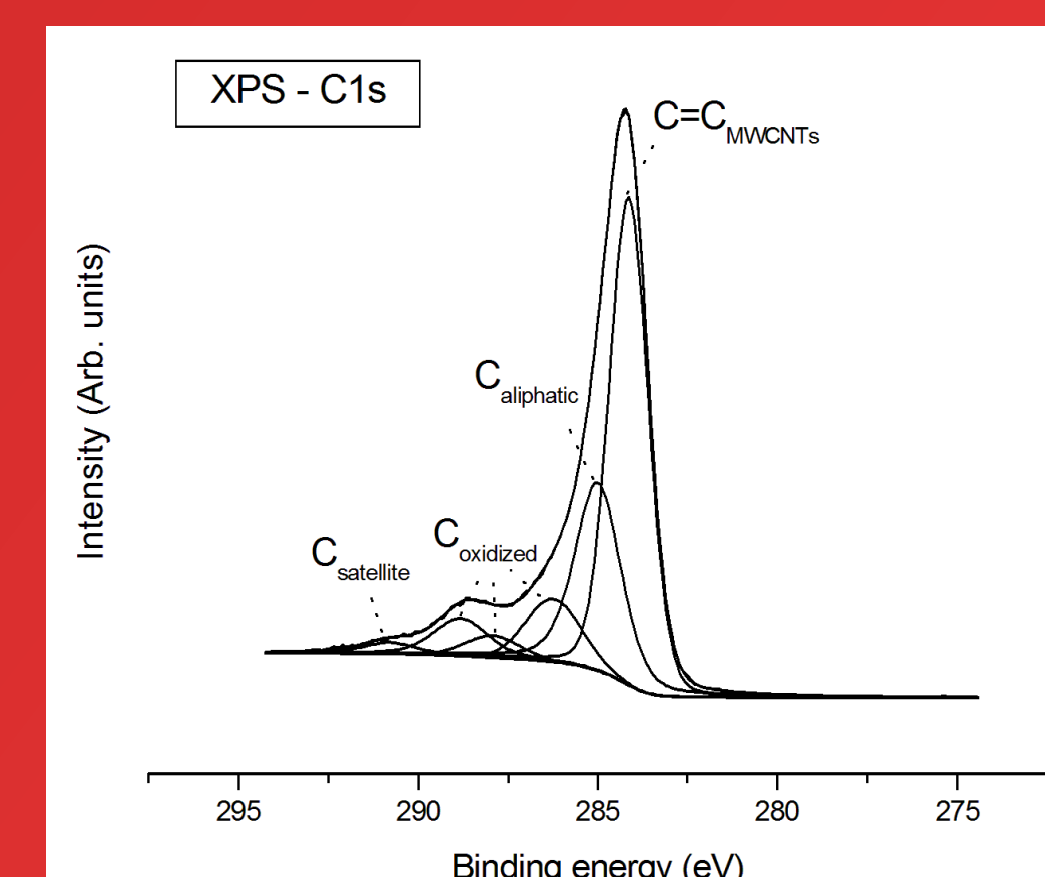
(C) **In vitro hydroxyapatite surfacial growth: 7 days immersion in 30 mL of a Simulated Body Fluid at 37°C and pH 7.25**



Results and discussion

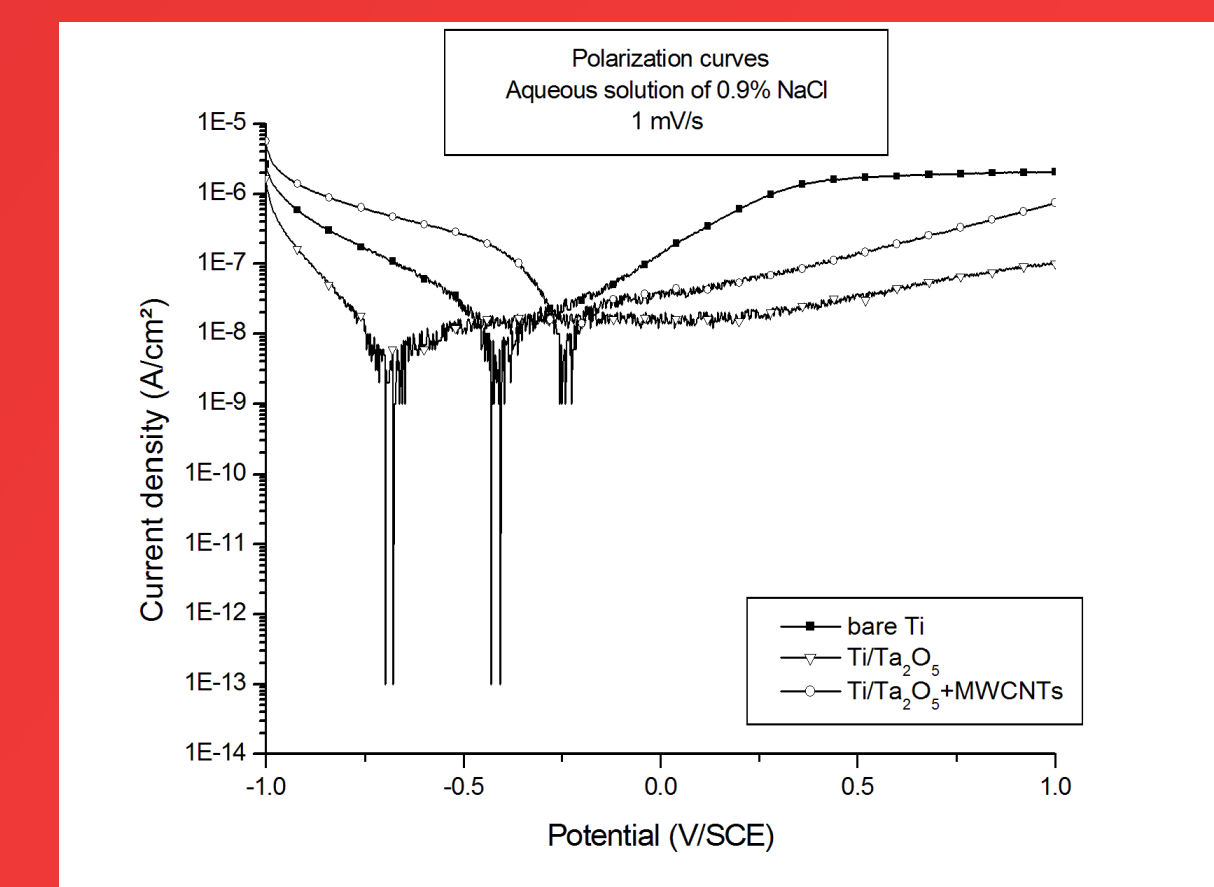
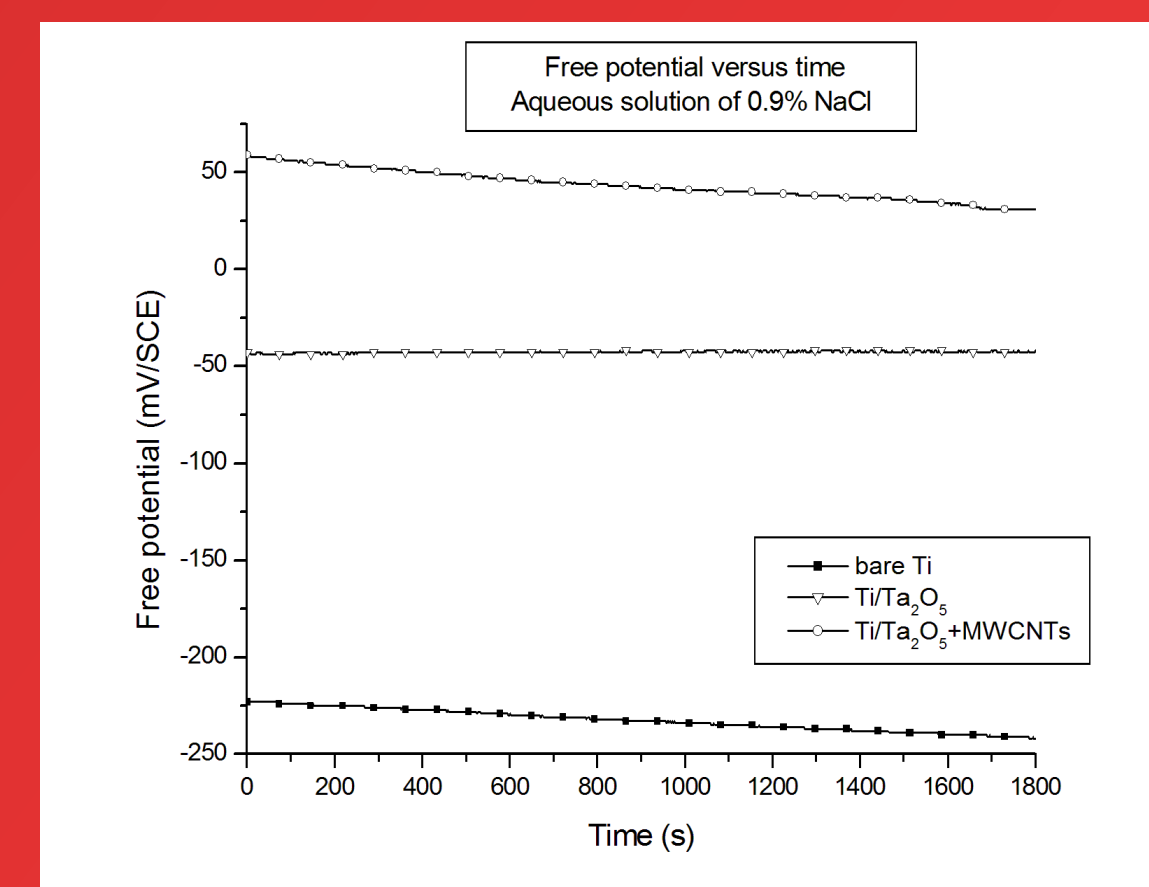
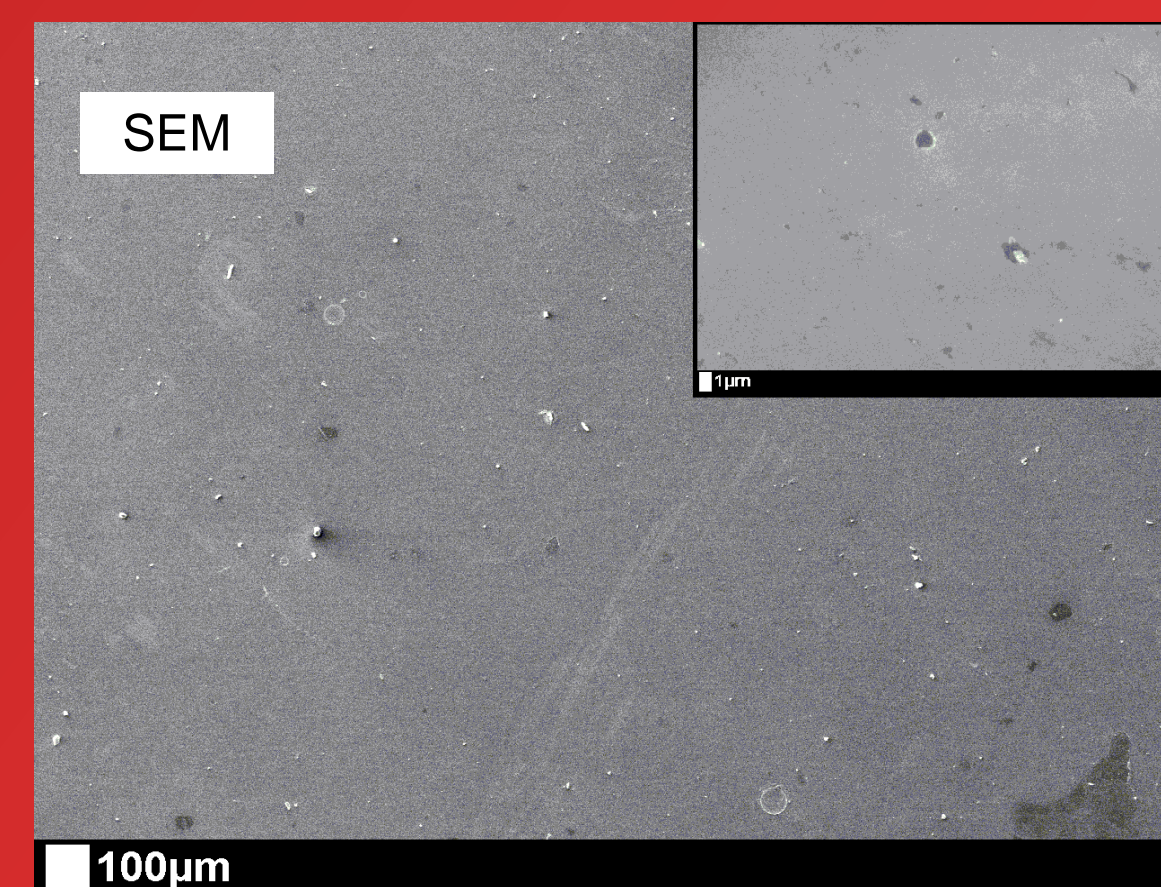
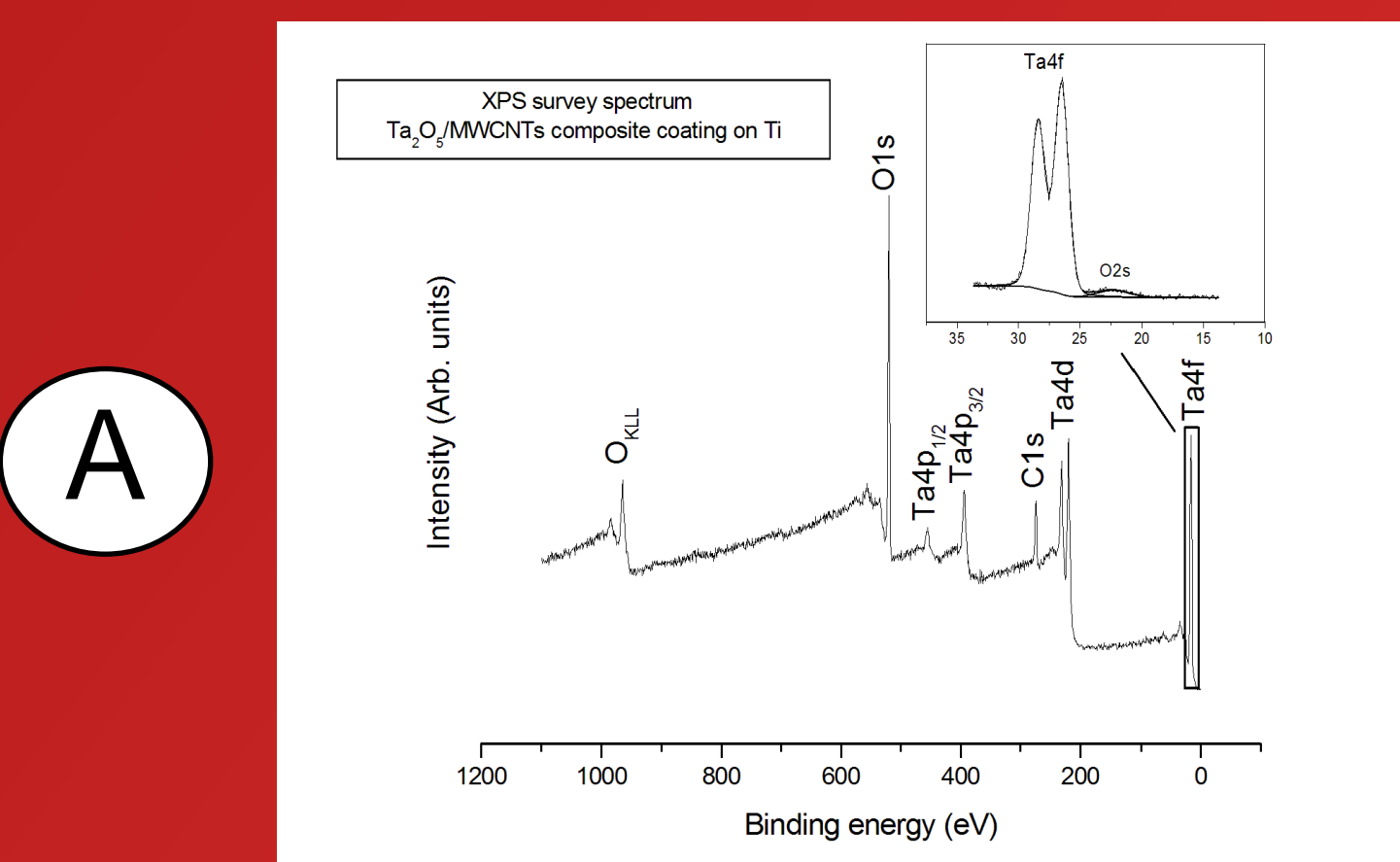
MWCNTs oxidative treatment

- **Optimized procedure:** oxidation in a 0.1 M KMnO₄/H₂SO₄ mixture at 60°C during 2 h
- ⇒ MWCNTs are soluble in abs. EtOH
- ⇒ Oxidation of MWCNTs is confirmed by XPS (C1s signal)
- ⇒ A global moderate shortening of the tubes is observed (length distributions out of TEM characterizations)



Sol-gel co-deposition of Ta₂O₅/MWCNTs composite coatings on Ti (A)

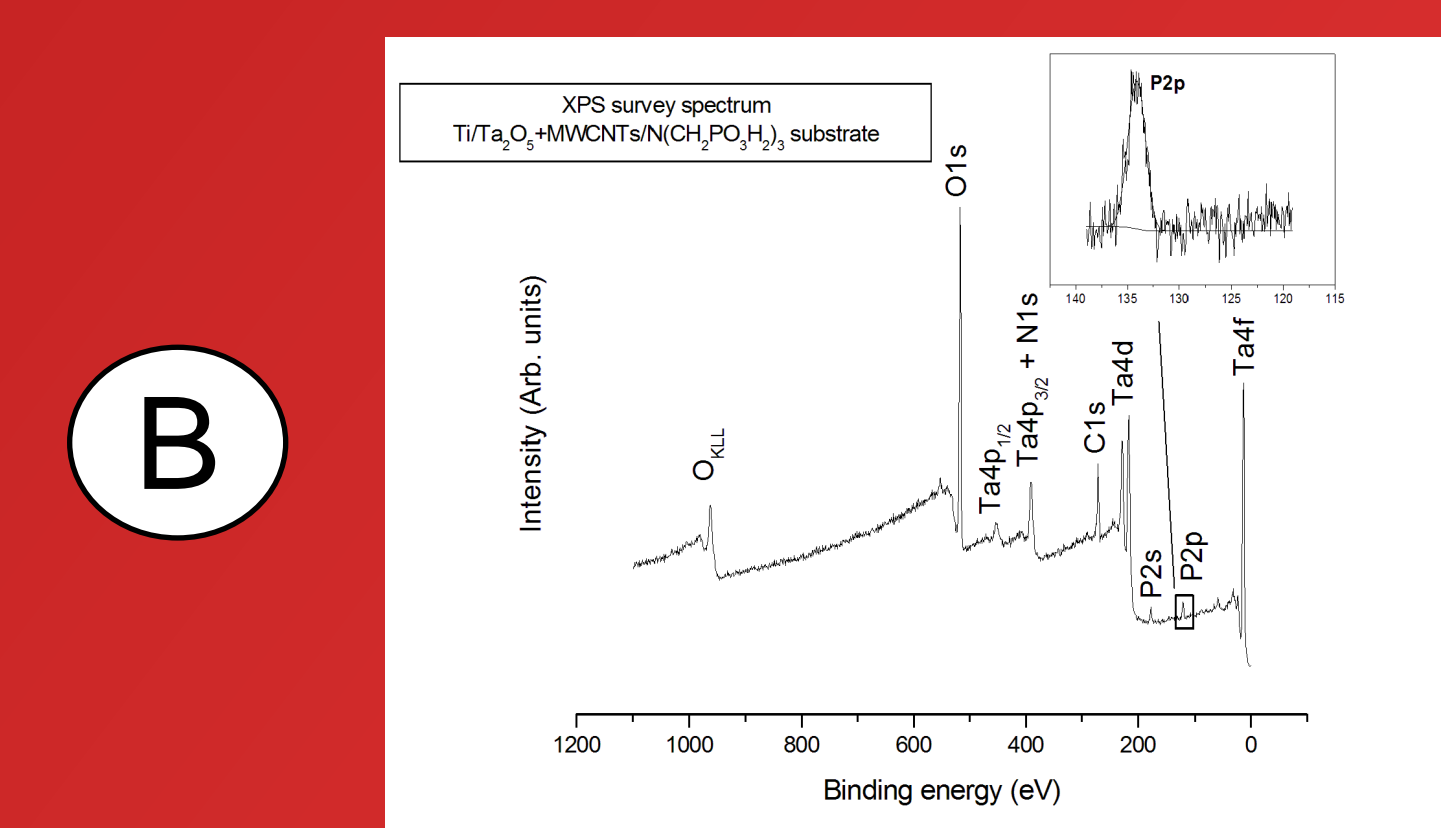
- Formation of **uncracked, adherent and homogeneous deposits** (XPS, SEM)
- **Passivation and high corrosion resistance** are observed with composite coatings (free potential, polarization curves)



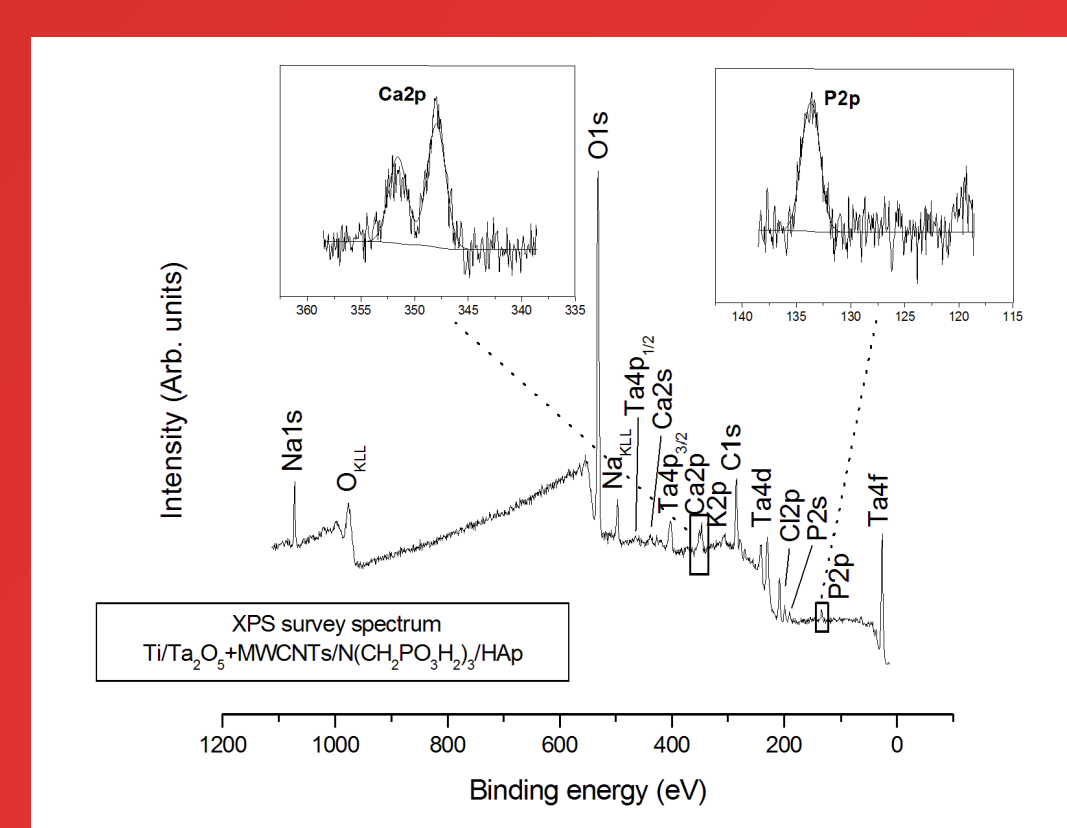
A

- ⇒ The optimized procedure allows the preparation of **high quality Ta₂O₅/MWCNTs composite coatings with great morphological, structural and adherent characteristics.**

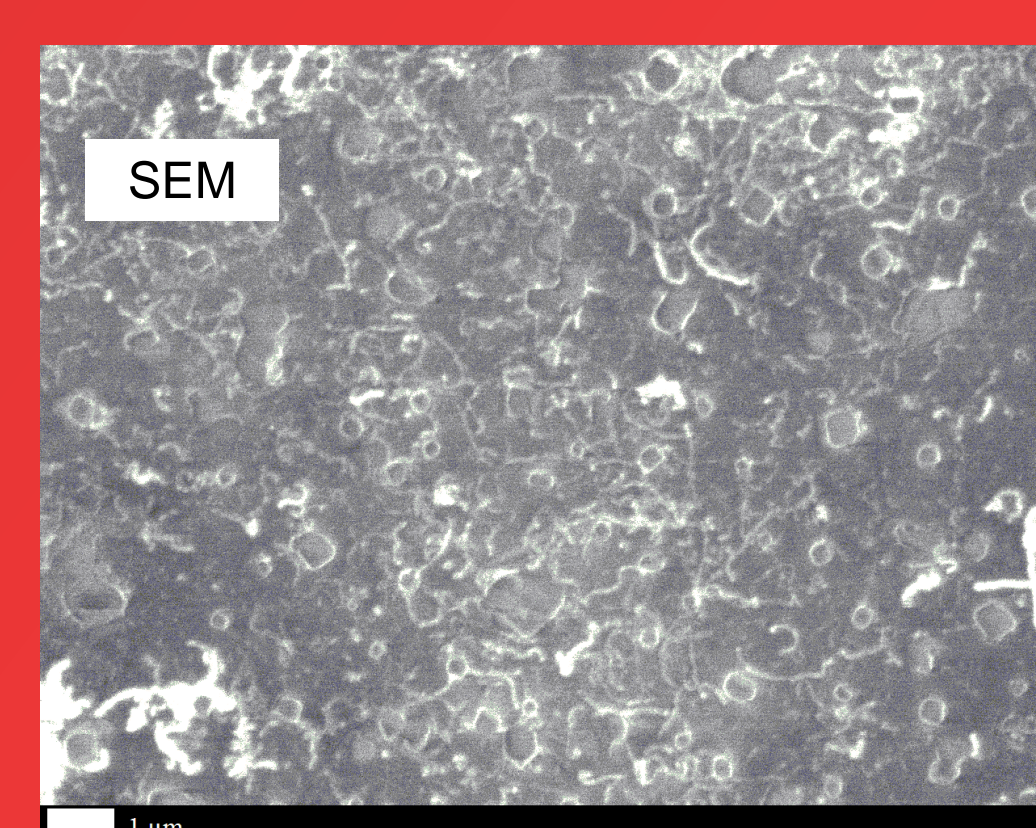
Functionalization with a molecular film of amino-tris-methylene phosphonic acid (B) and *in vitro* hydroxyapatite growth on a "completely-functionalized substrate: Ti/Ta₂O₅+MWCNTs/N(CH₂PO₃H₂)₃ (C)



B



C



- ⇒ The presence of phosphonic acid molecules and hydroxyapatite is confirmed by XPS survey spectra.
- ⇒ SEM characterizations of « completely-functionalized » substrates reveal an **important density** of hydroxyapatite crystals with a **particularly well defined crystallinity** (Ø ~ 0.5 μm).

Conclusions and perspectives

- The considered approach allows the formation of **highly homogeneous, adherent and cracks-free tantalum-based deposits** on titanium which are particularly **resistant to corrosion**.
- The composite coating made of oxidized MWCNTs dispersed in a Ta₂O₅ matrix, combined with the presence of surfacial phosphonic acid functions, leads to **an important reinforcement of the Ti substrate's bioactivity** through the *in vitro* formation of high quality hydroxyapatite crystals.
- **Perspectives:** *in vitro* tests of proliferation and adhesion of osteoblasts, preparation of Ta₂O₅/MWCNTs composites on titanium and its alloys through electro(co)deposition, ...

References

- [1] M. Geetha, A.K. Singh, R. Asokamani, A.K. Gogia, *Prog. Mater. Sci.* **2009**, *54*, 397-425; N. Tran, T.J. Webster, *Wiley Interdiscip. Rev. Nanomed. Nanobiotechnol.* **2009**, *1*, 336-351.
- [2] C. Arnould, T.I. Koranyi, J. Delhalle, Z. Mekhalif, *J. Colloid Interf. Sci.* **2010**, *344*, 390-394; V.K. Balla, S. Banerjee, S. Bose, A. Bandyopadhyay, *Acta Biomater.* **2010**, *6*, 2329-2334.
- [3] P.J.F. Harris, *Inter. Mater. Rev.* **2004**, *49*, 31-43; N. Narita, Y. Kobayashi, H. Nakamura, K. Maeda, A. Ishihara, T. Mizoguchi, Y. Usui, K. Aoki, M. Simizu, H. Kato, H. Ozawa, N. Udagawa, M. Endo, N. Takahashi, N. Saito, *Nano Lett.* **2009**, *9*, 1406-1413.
- [4] C. Arnould, C. Volcke, C. Lamarque, P.A. Thiry, J. Delhalle, Z. Mekhalif, *J. Colloid Interf. Sci.* **2009**, *336*, 497-503.