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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 plateforms 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 Ta_2O_5-based surface. The utilization of such **multifunctional phosphonic acid molecules** is of particular interest, as some $-PO_3H_2$ 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 Ta_2O_5/MWCNTs composite coatings on Ti substrates: optimized treatment**

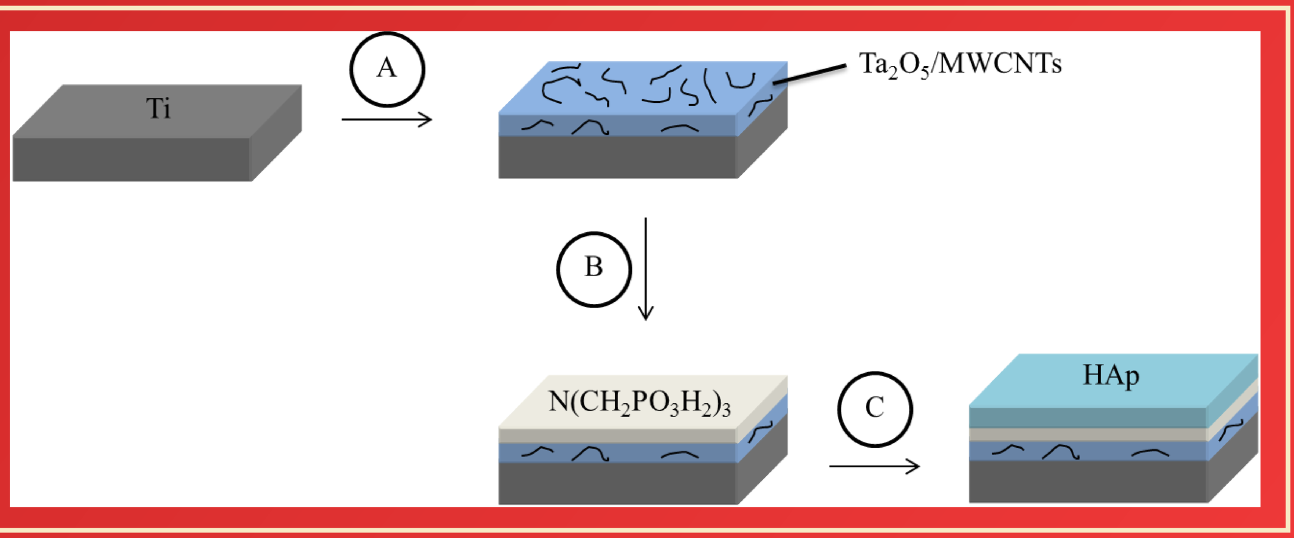
⇒ **10 min immersion in a sol-gel solution** made of 4.0 mL abs. EtOH, 0.2 mL of HCl (acid catalyst), and 8.0 mg of oxidized MWCNTs

⇒ **10 min gradual hydrolysis** in distilled water

⇒ **3 min drying at 300°C**

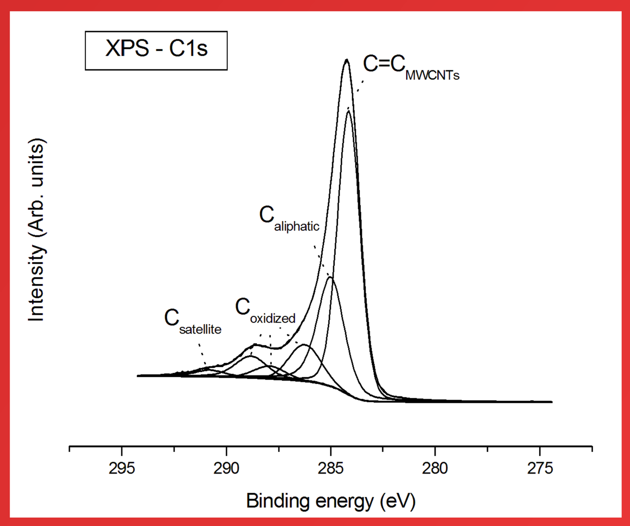
(B) **Grafting of an amino-tris-methylene phosphonic acid layer**: **1 h immersion** in a 10^{-3} M $N(CH_2PO_3H_2)_3$ aqueous solution at 25°C and pH~1

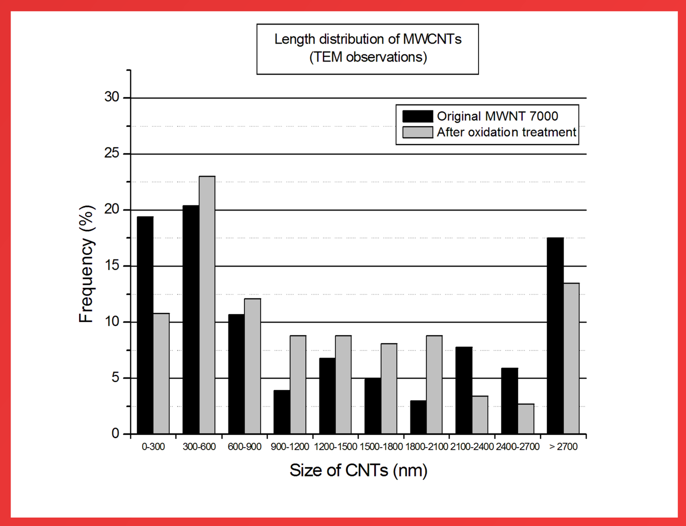
(C) *In vitro* **hydroxyapatite surfacial growth**: **7 days immersion** in 30 mL of a **Simulated Body Fluid** at 37°C and pH 7.25



Results and discussion

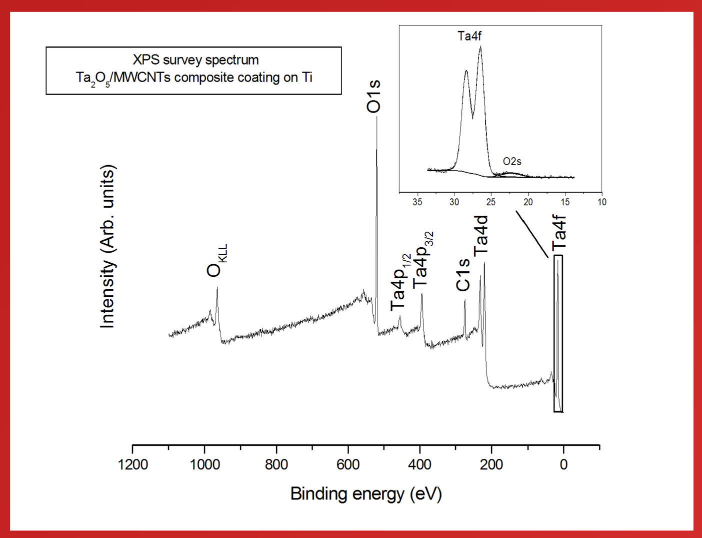
- **MWCNTs oxidative treatment**
  - **Optimized procedure**: oxidation in a **0.1 M $KMnO_4/H_2SO_4$ mixture at 60°C during 2 h**
    - ⇒ MWCNTs are soluble in abs. EtOH
    - ⇒ Oxidation of MWCNTs is confirmed by XPS (C1s signal)
    - ⇒ A global moderate shortening of the tubes is observed (length distributions out of TEM characterizations)

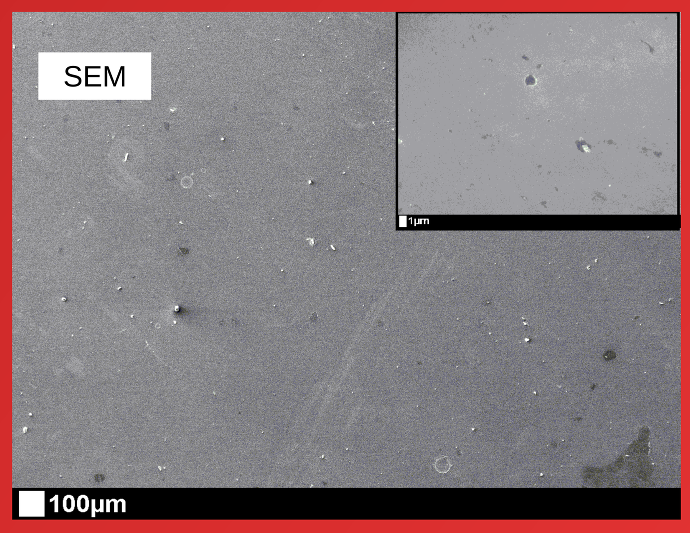


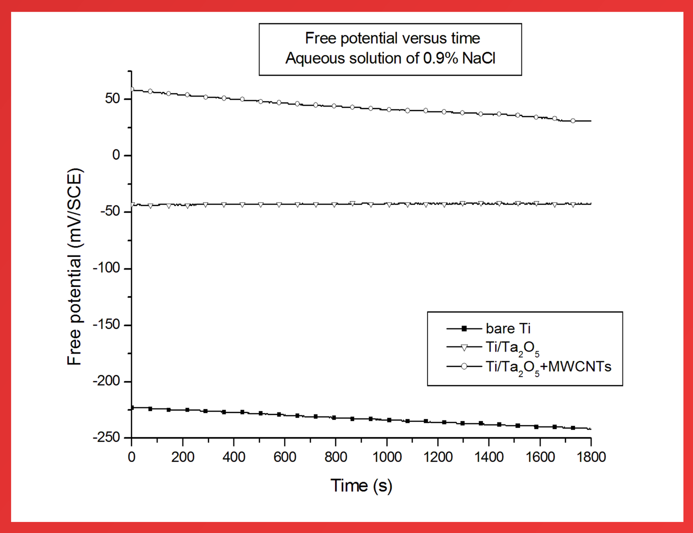


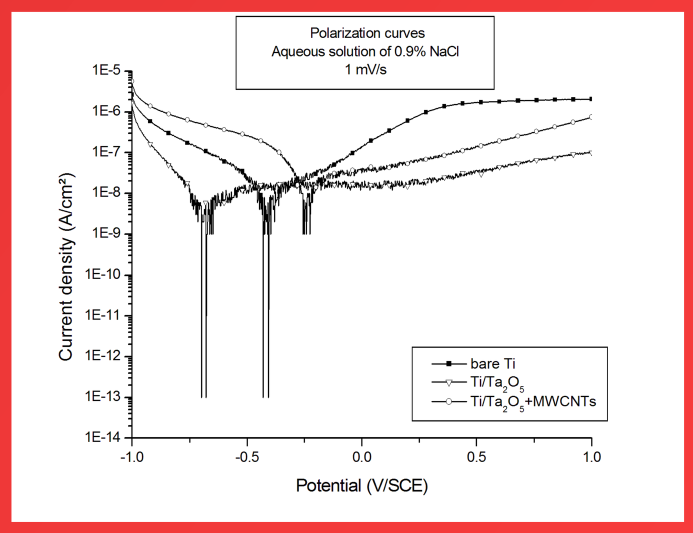
- **Sol-gel** co-deposition of **Ta_2O_5/MWCNTs composite coatings** on Ti **(A)**
  - Formation of **uncracked, adherent and homogeneous deposists** (XPS, SEM)
  - **Passivation and high corrosion resistance** are observed with composite coatings (free potential, polarization curves)

A





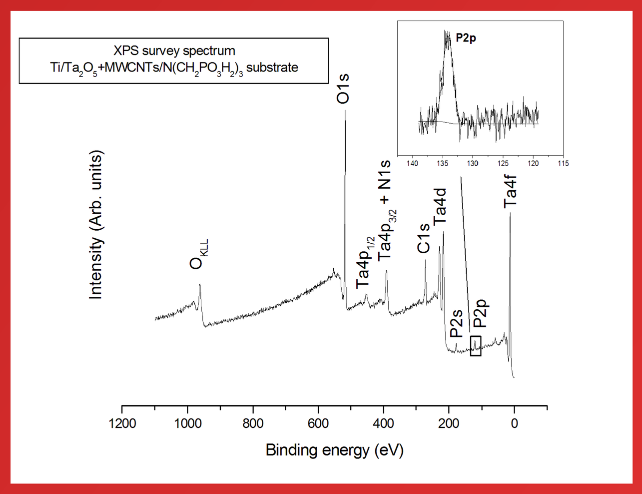




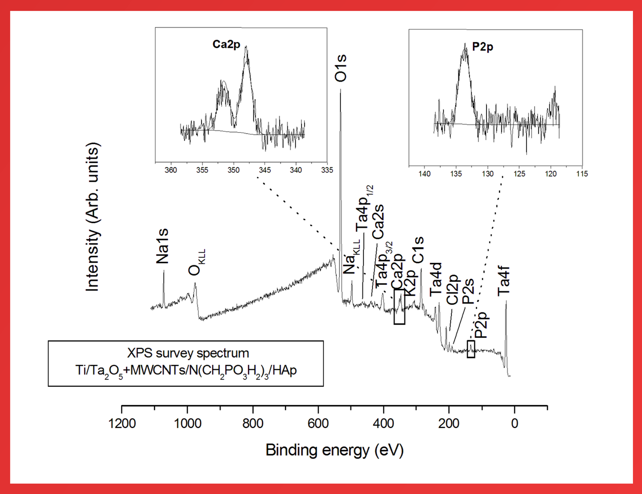
⇒ The optimized procedure allows the preparation of **high quality Ta_2O_5/MWCNTs composite coatings with great morphological, structural and adherent characteristics**.

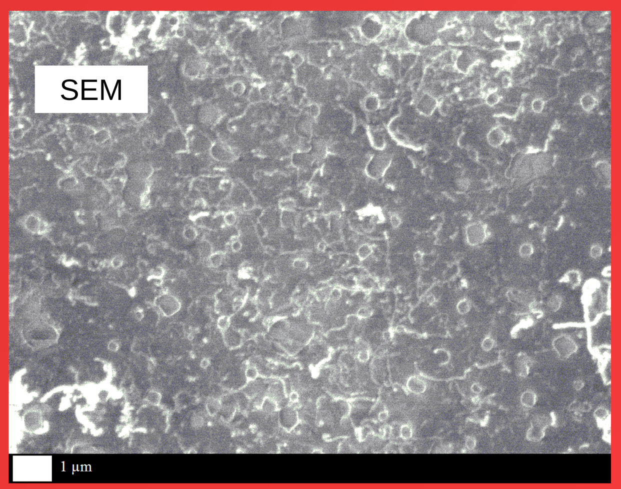
- Functionalization with a molecular film of amino-tris-methylene **phosphonic acid (B)** and ***in vitro* hydroxyapatite growth** on a "completely-functionalized substrate: Ti/Ta_2O_5+MWCNTs/$N(CH_2PO_3H_2)_3$ **(C)**

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 Ta_2O_5 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 Ta_2O_5/MWCNTs composites on titanium and its alloys through electro(co)deposition, …

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