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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, inertia to human body, corrosion resistance, … However, toxicity of certain alloys elements (tin in niobium, …) long-term degradation and weak osseointegration remain problematic features [1].
- One solving approach is to form 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].
- Multilayer 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
- 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
- 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
- In vitro hydroxyapatite superficial 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)
  - 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)
  - 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 (D ~ 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 surficial 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 composite on titanium and its alloys through electro(co)deposition.

References

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