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Sol–gel synthesis of tantalum oxide and phosphonic acid-modified carbon nanotubes composite coatings on titanium surfaces

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A B S T R A C T

Carbon nanotubes used as fillers in composite materials are more and more appreciated for the outstanding range of accessible properties and functionalities they generate in numerous domains of nanotechnologies. In the framework of biological and medical sciences, and particularly for orthopedic applications and devices (prostheses, implants, surgical instruments, …), titanium substrates covered by tantalum oxide/carbon nanotube composite coatings have proved to constitute interesting and successful platforms for the conception of solid and biocompatible biomaterials inducing the osseous regeneration processes (hydroxyapatite growth, osteoblasts attachment). This paper describes an original strategy for the conception of resistant and homogeneous tantalum oxide/carbon nanotubes layers on titanium through the introduction of carbon nanotubes functionalized by phosphonic acid moieties ($-P(=O)(OH)_2$). Strong covalent C–P bonds are specifically inserted on their external sidewalls with a ratio of two phosphonic groups per anchoring point. Experimental results highlight the stronger "tantalum capture agent" effect of phosphonic-modified nanotubes during the sol–gel formation process of the deposits compared to nanotubes bearing oxidized functions ($-OH$, $-C=O$, $-C(=O)OH$). Particular attention is also paid to the relative impact of the rate of functionalization and the dispersion degree of the carbon nanotubes in the coatings, as well as their wrapping level by the tantalum oxide matrix material. The resulting effect on the in vitro growth of hydroxyapatite is also evaluated to confirm the primary osseous bioactivity of those materials. Chemical, structural and morphological features of the different composite deposits described herein are assessed by X-ray photoelectron spectroscopy (XPS), scanning (SEM) and transmission (TEM) electronic microscopies, energy dispersive X-rays analysis (EDX) and peeling tests.

1. Introduction

The use and impact of titanium (Ti) as bulk material in biomedical sciences has been increasingly investigated and developed those recent years. Thanks to their very interesting mechanical and biochemical properties (appropriate Young modulus and density, high solidity and fatigue strength, reinforced biocompatibility, inertness to human body, corrosion resistance, …), titanium-based biomaterials can be exploited for the design of various surgical instruments as well for the elaboration of cardiovascular, dental and osseous implants and prostheses [1–6]. However, the lack of strong bioactive properties — especially osseointegration abilities for orthopedic devices — combined with long-term degradation effects under physiological conditions and potential toxicity of alloying elements (nickel in Nitinol, vanadium in Ti–6Al–4V, …) require the development of specific solving strategies [7–12]. For this purpose, a successful approach based on the deposition of thin tantalum (Ta) layers on the titanium surfaces has been reported. Indeed, tantalum as coating material reinforces the biocompatibility and bioactivity features of the titanium platforms, while increasing their corrosion resistance and bringing them radio-opacity (interesting for medical imagery applications) [13–16].

In an attempt to globally strengthen the tantalum deposit (internal cohesion, adherence with the titanium surface), we intend to take advantage of the exceptional mechanical properties of multiwalled carbon nanotubes (MWCNTs) by incorporating them in so-called composite coatings [17]. Moreover, CNTs integrated into such layers are able to bio-mimic the collagen fiber structure (organic component of the osseous matrix), which can also specifically increase the interactions with osteoblasts and osteoclasts (osseous body cells) and favor hydroxyapatite (inorganic component of the osseous matrix) formation on the surface, which are the first steps of the integration process of a bone implant into the human body [18,19]. To this extent, the sol–gel co-deposition technique has been particularly praised for its practical easiness and its use of non-expensive materials [20–25].

From a general point of view, the main challenge for the design of high-quality composite biomedical devices based on CNTs lies in the control of their incorporation as reinforcements. A first key parameter involves thus the quality of their global wrapping by the matrix material

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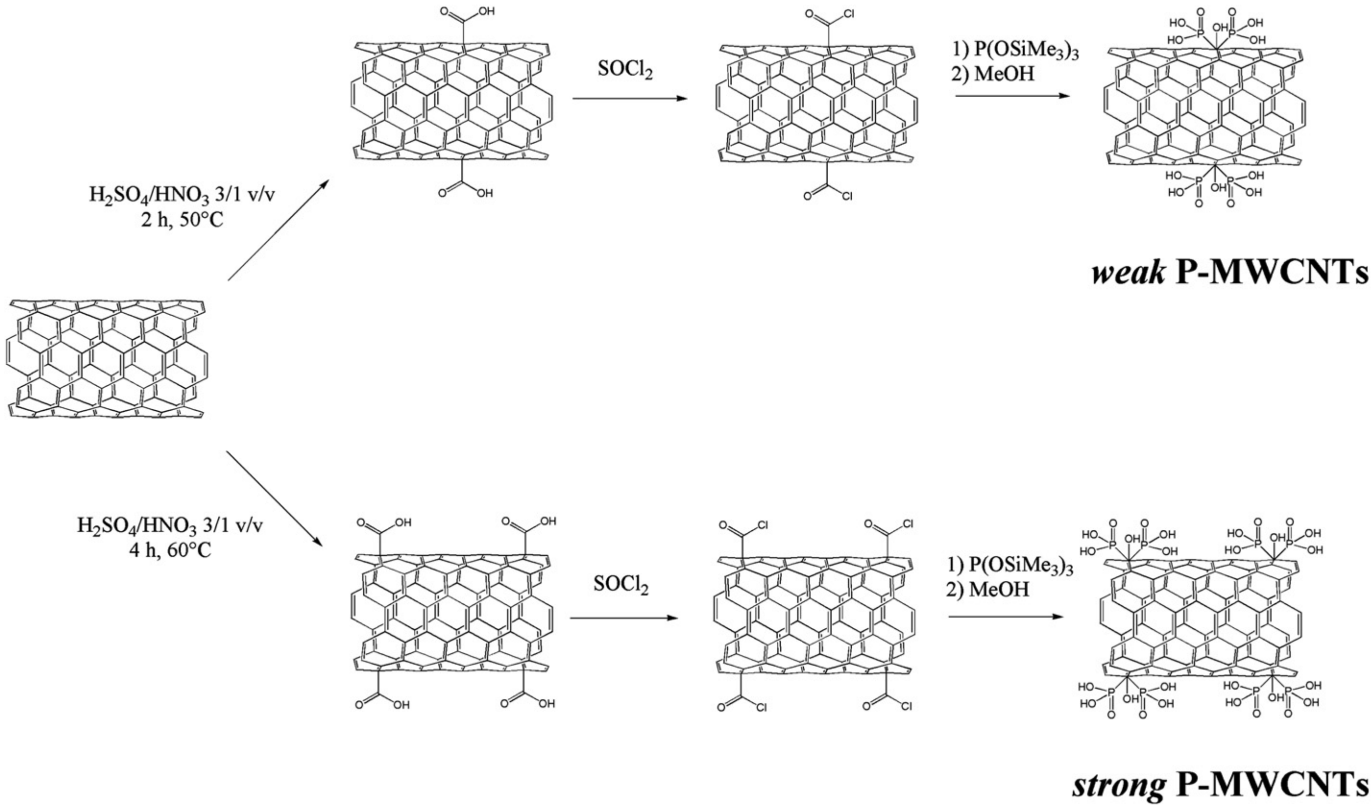

Fig. 1. Synthesis protocols of *weak* P-MWCNTs (up) and *strong* P-MWCNTs (down) from crude multiwalled carbon nanotubes (MWNT 7000, Nanocyl).

(here Ta_2O_5). Several publications in the literature already focused their attention on this very particular aspect, and especially on the coating and/or filling of the CNTs with metal and metal oxide nanoparticles (NP) or nanolayers as matrix. For instance, Ma and Zhang reported the coverage of multiwalled carbon nanotubes (MWCNTs) by Au-NP for electrochemical sensing applications [26]. Tan et al. performed the preparation of magnetic nanocomposites by depositing γ-Fe_2O_3 nanoparticles on both inner and outer surfaces of MWCNTs [27], while Liu et al. managed to synthesize Fe_3O_4-MWCNT nanocomposites [28]. Gao et al. succeeded for their part in covering MWCNTs with a 5–10 nm layer of TiO_2 through a surfactant wrapping sol–gel process, leading to high-performance semi-conducting devices [29]. Recently, our group also managed to selectively and uniformly decorate MWCNTs with copper and nickel nanocrystals for energy-related purposes [30,31].

An important attention must also be paid to the quality of the CNT dispersion into the matrix component of the composite. In many cases, this is achieved through the control of their dispersion in a solution-phase during the preparation process of the material, for which different approaches are described in the literature. Crude CNTs can be dispersed in an appropriated solvent, which is conveniently selected following the Hansen Solubility Parameter (HSP) theory [32,33]. The use of well-chosen surfactants or additives can also be exploited, but those molecules are sometimes considered as impurities and cannot always be removed posteriorly from the material without losing a proper

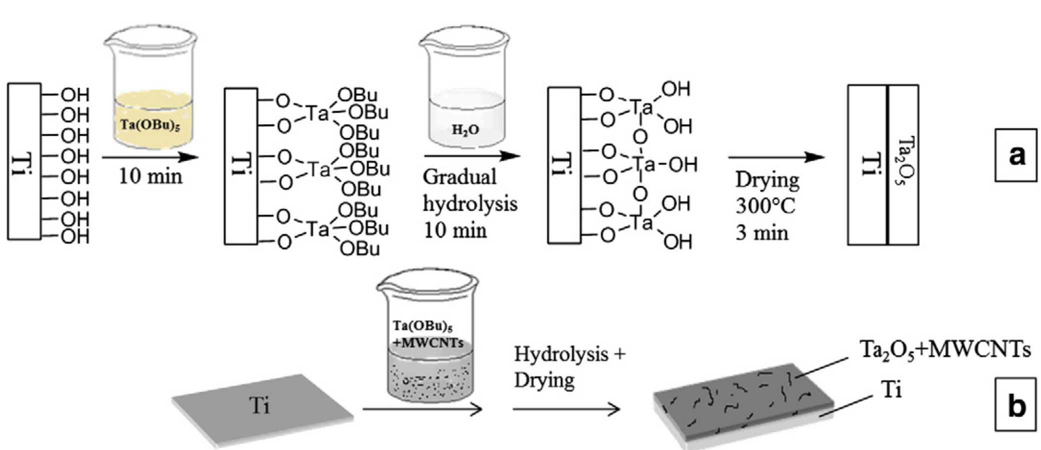

Fig. 2. Principles of the sol–gel processes: (a) sol–gel deposition of Ta_2O_5 on Ti and (b) sol–gel co-deposition of Ta_2O_5 and MWCNTs on Ti.