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羟基磷灰石/碳纳米管和氧化钛纳米管复合生物材料的制备与表征

Preparation and Characterization of the HA/MWNTs and HA/TiO_2 Nanotubes Composite Biomaterials

赵彦荣

指导教师姓名：林 昌 健 教授

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Preparation and Characterization of the HA/MWNTs and HA/TiO_2 Nanotubes Composite Biomaterials

A Dissertation Submitted to the Graduate School in Partial Fulfillment of the Requirements for the Degree of Master of Science

By

Yan-rong Zhao

Directed by **Prof. Chang-Jian Lin**

Department of Chemistry, Xiamen University

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目　录

Contents

中文摘要

羟基磷灰石（HA）是人体骨骼和牙齿的最主要无机成分，人工合成的 HA 具有良好的生物相容性和生物活性，但 HA 脆性大、强度低，抗折强度和断裂韧性指标均低于人工致密骨的特性，限制了它在临床的实际应用。医用金属钛表面涂覆 HA 可结合金属材料的良好力学性能和 HA 良好生物性能，已被广泛地用作人体硬组织替代材料。然而，HA 与钛基底热膨胀系数失配造成的残余应力，降低了涂层与基底之间的结合力，临床应用中常出现涂层脱落或植入体松动现象。二氧化钛纳米管具有良好的生物活性、抗腐蚀性及耐磨损性，因此，发展 HA/二氧化钛纳米管复合增强体，可望起到增韧补强作用，提高 HA 涂层的力学性能，具有重要的临床应用价值。磷酸钙骨水泥（CPC）是一种重要的硬组织修复材料，在临床上已广泛应用，如何进一步提高 CPC 的力学性能，解决其抗压抗折强度低等力学问题，仍面临很大的挑战，而碳纳米管（CNTs)具有独特的力学性能，因此发展 CPC/CNTs 复合材料，有望获得力学性能优异的纤维类增强材料，而其中的关键问题是需要解决 CPC/CNTs 复合材料的生物安全性问题。

针对上述关键问题，本文采用水热法制备了HA/TiO_2纳米管和HA/MWNTs复合增强体，为获得力学性能优良的硬组织替代材料和骨水泥硬组织修复材料提供基础。主要研究结果和进展如下：

1. 采用水热法，以 P-25 为原料，保持固液比 1.5 g/140 mL，在 10 mol/L 的 NaOH 溶液中水热反应 48 h，成功制备了二氧化钛纳米管粉体，纳米管管径 8-10 nm，长度约几个微米；
2. 首次采用电泳沉积方法，在钛表面涂覆HA/二氧化钛纳米管梯度复合涂层，经过 700℃煅烧处理 2 h，所制备的HA/TiO_2纳米管梯度复合涂层剪切力达到 32.97±2MPa(一般 HA 涂层与基底之间的剪切力为 19.82±3MPa），接近与人体骨的承载强度(35MPa)；大载荷划痕测试结果表明，这种梯度复合涂层与Ti基底之间的结合力比纯HA涂层与Ti基底之间的结合力提高了约 2.3 倍。考察了煅烧温度对电泳沉积涂层与基底之间的结合力的影响，结果表明 700℃煅烧 2h可有效地对HA涂层材料实现增韧补强作用；
3. 采用化学共沉淀结合水热后处理，实现了 HA/MWNTs 复合生物材料的

宏量制备，当复合材料中碳纳米管含量占15%时，MWNTs与HA发生充分作用，可在MWNTs表面覆盖一层紧密的纯纳米HA晶粒膜层。经700℃煅烧后，发现HA与MWNTs的结合进一步强化，在MWNTs表面形成更加致密均匀的HA膜层；

4. 体外细胞培养实验表明，含15%MWNTs的HA/MWNTs复合材料没有明显毒性，具有良好的生物相容性。

关键词：羟基磷灰石；二氧化钛纳米管；碳纳米管；水热合成；电泳沉积；力学性能；生物性能

Abstract

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) is the main inorganic component in natural bone and tooth. The synthetic form of HA has good biocompatibility and bioactivity, unfortunately, its mechanical properties including brittleness, low strength, flexural strength and fracture toughness all are lower than that of natural bone, which inhibits its clinical applications. Conducting HA coatings on biomedical titanium have been widely used for human hard tissue substitute materials, based on a combination of good mechanical properties of titanium and the excellent biological properties of HA. However, mismatch of the coefficient of thermal expansion of HA and Ti substrate may cause a residual stress, which reduced the bonding between the coating and substrate, and result in a failure of implantation in clinical application. TiO_2 nanotubes have good biological activity, corrosion resistance and wear resistance, therefore, the development of HA/TiO_2 nanotube composite reinforcements has an important clinical value, for improving toughening and strengthening the mechanical properties of HA coating. Calcium phosphate cement (CPC) is an important hard-tissue repair material, it has been widely applied in clinical practices. How to further improve the mechanical properties of CPC to resolve its mechanical problems, such as compressive strength and low bending strength, it still faces significant challenges. It is expected that the development of CPC/CNTs composite materials may be helpful to obtain fiber reinforced materials with excellent mechanical properties according to the unique mechanical properties of carbon nanotubes (CNTs), in which, the most concerned issue is the toxity and biosafety of the CPC/CNTs composites in medical application.

In response to these key issues, in this thesis we prepared HA/TiO_2 nanotubes and HA /MWNTs composite reinforcements by hydrothermal reaction, in order to obtain hard tissue replacement materials and bone cement hard tissue repair materials with excellent mechanical properties. The main findings and progress are as follows:

1. The TiO_2 nanotubes powders with the diameter of 8-10 nm and the length of few microns were successfully prepared through hydrothermal synthesis, by using P-25 as raw materials, maintained solid-liquid ratio 1.5 g/140 mL, in 10 mol/L of NaOH solution for 48 h；
2. The electrophoretic deposition method had been developed firstly to prepare a composite coating of HA/TiO_2 nanotubes, after calcined treatment 2 h at 700 ℃, the shear stress between prepared HA/TiO_2 composite coating and substrate titanium reached 32.97±2MPa (generally the shear stress between the HA coating and substrate is 19.82 ± 3MPa), which closely to the bearing strength of human bones (35MPa). The load scratch test results showed that the binding increase by 2.3 times compared to the binding between the composite coating and Ti substrate to pure HA coating and Ti substrate. The effect of calcination temperature on the binding between the electrophoretic deposition coating and substrate was studied. It is revealed that it can effectively improve toughening and strengthening of the coatings when the calcination temperature is at 700℃；
3. The chemical co-precipitation and hydrothermal post-processing were combined to achieve the preparation of HA/MWNTs composite in scale. It is revealed that the MWNTs are well coated with a dense nano-HA particles when the content of MWNTs is about 15%(by mass). After being calcinated at 700℃, the bonding between HA and MWNTs is further strengthened, a more dense and uniform HA film is obtained on the surface of MWNTs；
4. The in vitro cell culture demonstrates that the prepared HA/MWNTs nano-composites with 15% (by mass) of MWNTs exhibit with no significant toxicity and show a good biocompatibility.

Key words: hydroxyapatite; titania nanotubes; carbon nanotubes; hydrothermal synthesis; electrophoretic deposition; mechanical properties; biological properties