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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/TiO₂ Nanotubes Composite Biomaterials

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**Preparation and Characterization of the HA/MWNTs and
HA/TiO₂ Nanotubes Composite Biomaterials**



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

By

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目 录

中文摘要.....	I
英文摘要.....	III
第一章 绪论	1
§1.1 生物材料简介	1
§1.2 三大硬组织修复材料	2
1.2.1 生物医用金属材料.....	2
1.2.2 医用高分子材料.....	3
1.2.3 生物陶瓷材料.....	4
§1.3 羟基磷灰石复合材料	6
1.3.1 羟基磷灰石/无机复合材料.....	7
1.3.2 羟基磷灰石/医用高分子复合材料.....	7
1.3.3 羟基磷灰石涂层/医用金属复合材料.....	7
§1.4 医用钛表面涂覆技术	7
1.4.1 物理涂覆.....	8
1.4.2 化学涂覆.....	9
1.4.2.1 爆炸喷涂法.....	9
1.4.2.2 溶胶凝胶法.....	9
1.4.2.3 化学气相沉积.....	9
1.4.2.4 电化学沉积.....	10
1.4.2.5 电泳沉积.....	10
§1.5 磷酸钙骨水泥	11
§1.6 本论文的研究目的和设想	13
参考文献.....	15

第二章 实验方法和仪器 24

§2.1 实验方法 24

2.1.1 水热合成技术 24

2.1.2 电泳沉积技术 25

§2.2 复合材料理化性质的表征 27

2.2.1 扫描电子显微镜(SEM) 27

2.2.2 透射电子显微镜和高分辨透射电子显微镜(TEM & HRTEM) 27

2.2.3 X 射线粉末衍射(XRD) 29

2.2.4 红外吸收光谱 (IR) 29

2.2.5 激光拉曼光谱 (Raman) 29

2.2.6 热重分析技术 30

2.2.7 倒置显微镜 30

§2.3 复合材料力学性能及生物性能的表征 31

2.3.1 细胞培养 31

2.3.2 细胞接种与观测 31

2.3.3 粘结-拉伸实验 32

2.3.4 大载荷划痕测试 32

参考文献 34

第三章 水热合成二氧化钛纳米管 35

§3.1 前言 35

§3.2 二氧化钛纳米管的制备 36

3.2.1 二氧化钛纳米管的制备过程 36

3.2.2 水热合成过程的影响因素 36

3.2.2.1 反应温度 36

3.2.2.2 反应时间 37

3.2.2.3 固液比 38

3.2.2.4 不同原料.....	39
3.2.3 形貌分析.....	39
3.2.4 成分分析.....	40
§3.3 水热合成机理探讨.....	41
§3.4 本章小结.....	42
参考文献.....	43

第四章 羟基磷灰石/二氧化钛纳米管复合涂层电泳沉积及表征46

§4.1 电泳沉积原理.....	47
4.1.1 基于 DLVO 理论的沉积机理.....	47
§4.2 电泳沉积复合涂层条件优化.....	49
4.2.1 悬浮液的 pH 值.....	49
4.2.2 溶剂及悬浮液浓度.....	49
4.2.3 陈化时间.....	50
4.2.4 悬浮液的分散.....	50
4.2.5 电压和沉积时间的选择.....	50
4.2.6 基体预处理.....	51
4.2.6.1 电化学刻蚀.....	51
4.2.6.2 酸刻蚀.....	51
4.2.6.3 碱刻蚀.....	51
4.2.7 热处理.....	52
§4.3 HA/TiO₂纳米管梯度复合涂层的制备.....	53
§4.4 梯度复合涂层的表征.....	57
4.4.1 XRD 表征.....	57
4.4.2 梯度复合涂层的力学性能表征.....	57
4.4.2.1 粘结拉伸实验.....	57
4.4.2.2 大载荷划痕测试.....	58
4.4.3 生物性能表征.....	59
§4.5 本章小结.....	61

参考文献:	62
第五章 HA/MWNTs 复合生物材料的制备及其表征	64
§5.1 前言	64
§5.2 碳纳米管的预处理	65
§5.3 碳纳米管的分散与表征	67
5.3.1 MWNTs 的分散	67
5.3.2 纯化碳纳米管的表征	67
§5.4 羟基磷灰石/碳纳米管复合材料的制备	69
§5.5 羟基磷灰石/碳纳米管复合材料的表征	69
5.5.1 形貌表征	69
5.5.2 成分分析	72
5.5.3 生物性能表征	75
5.5.4 热重分析	76
§5.6 高温煅烧前后的羟基磷灰石/碳纳米管复合材料的研究	77
5.6.1 形貌表征	77
5.6.2 生物性能表征	80
§5.7 本章小结	82
参考文献	83
第六章 结论与展望	86
作者在攻读硕士学位期间发表与交流的论文	88
致谢	89

Contents

Abstract in Chinese	I
Abstract in English	III
Chapter 1 Introduction	1
§1.1 Brief Introduction to Biomaterials	1
§1.2 Three Hard Tissue Substitutes	2
1.2.1 Biomedical Metal.....	2
1.2.2 Biomaterials of Macromolecule.....	3
1.2.3 Bioceramics Materials	4
§1.3 Hydroxyapatite Composite	6
1.3.1 Hydroxyapatite/Mineral Composite	7
1.3.2 Hydroxyapatite/Biomedical Macromolecule	7
1.3.3 Hydroxyapatite/Biomedical Metal Composite	7
§1.4 Surface Modification of Titanium	7
1.4.1 Physical Methods	8
1.4.2 Chemical Treatment	9
1.4.2.1 Plasma Spray.....	9
1.4.2.2 Sol-Gel	9
1.4.2.3 Chemical Vapor Deposition	9
1.4.2.4 Electrochemical Deposition	10
1.4.2.5 Electrophoretic Deposition	10
§1.5 Calcium Phosphate Cement	11
§1.6 Objective and Plan of the Dissertation	13
Reference	15

Chapter 2 Instrument and Method Used in Experiment.....24

§2.1 Experimental methods24

2.1.1 Hydrothermal Synthesis Technology24

2.1.2 Electrophoretic Deposition Technology25

§2.2 Characterization of Physicochemical Properties of the Composites.....27

2.2.1 Scanning Electron Microscopy(SEM)27

2.2.2 Transmission Electron Microscopy(TEM)27

2.2.3 X-ray Diffraction(XRD)29

2.2.4 Infrared Spectroscopy(IR).....29

2.2.5 Raman Spectroscopy(Raman).....29

2.2.6 Thermal Gravity Analysis(TGA)30

2.2.7 Inverted Microscopy.....30

§2.3 Characterization of Mechanical Behavior and Biological Performance of

the Composites31

2.3.1 In Vitro Cell Culture Test31

2.3.2 Cell Culture and Observation.....31

2.3.3 Adhesive Strength Test32

2.3.4 Revetest Scratch Test.....32

Reference34

Chapter 3 Hydrothermal Synthesis of Titania Nanotubes 35

§3.1 Introduction35

§3.2 Preparation of Titania Nanotubes.....36

3.2.1 Preparation Process of Titania Nanotubes36

3.2.2 Influencing Factor of Hythermal Synthesis Process36

3.2.2.1 Reaction Temperature36

3.2.2.2 Reaction Time37

3.2.2.3 Solid-Liquid Ratio	38
3.2.2.4 Raw Material.....	39
3.2.3 Characterization of Morphology.....	39
3.2.4 Characterization of Composition	40
§3.3 Mechanism of Hythermal Synthesis Process	41
§3.4 Summary	42
Reference	43

Chapter 4 Preparation and Characterization of HA/Titania

Nanotubes Grade Composite Coating	46
§4.1 Mechanism of EPD	47
4.1.1 Mechanism Based on DLVO Theory	47
§4.2 Optimization the Conditon of EPD	49
4.2.1 pH Value of the Suspension.....	49
4.2.2 The Concentration and the Dispersant	49
4.2.3 Aged Time	50
4.2.4 Dispersion of the Suspension	50
4.2.5 Selecting of Potential and Time.....	50
4.2.6 Pretreatment of Substrate	51
4.2.6.1 Electrochemical Treatment.....	51
4.2.6.2 Acid Treatment	51
4.2.6.3 Alkali Treatment	51
4.2.7 Sintering	52
§4.3 Preparation of HA/Titania Nanotubes Grade Composite Coating.....	53
§4.4 Characterization of HA/Titania Nanotubes Grade Composite Coating ...	57
4.4.1 Characterization of Composition.....	57
4.4.2 Characterization of Mechanical Properties	57
4.4.2.1 Adhensive Strength Test	57
4.4.2.2 Revetest Scratch Test.....	58

4.4.3 Characterization of Biocompatibility	59
§4.4 Summary	61
Reference	62
Chapter 5 Preparation and Characterization of HA/MWNTs Composite.....	64
§5.1 Introduction	64
§5.2 Pretreatment of MWNTs	65
§5.3 Dispersion and Characterization of MWNTs	67
5.3.1 Dispersion of MWNTs	67
5.3.2 Characterization of MWNTs.....	67
§5.4 Preparation of HA/MWNTs Composite	69
§5.5 Characterization of HA/MWNTs Composite	69
5.5.1 Characterization of Morphology.....	69
5.5.2 Characterization of Composition	72
5.5.3 Characterization of Biocompatibility.....	75
5.5.4 TG-DTA Curve	76
§5.6 HA/MWNTs Composite Before and After Sintering.....	77
5.6.1 Characterization of Morphology.....	77
5.6.2 Characterization of Biocompatibility.....	80
§5.7 Summary	82
Reference	83
Chapter 6 Conclusions and Future Work	86
Publications and Conference Presentations	88
Acknowledgements.....	89

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/TiO₂ 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/TiO₂ 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 ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, 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 toxicity 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 TiO₂ 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/TiO₂ nanotubes, after calcined treatment 2 h at 700 °C, the shear stress between prepared HA/TiO₂ 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°C;
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°C, 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

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