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羟基磷灰石涂层的电化学可控制备  
及形成机理研究

**Study on Electrochemically Controllable  
Preparation of Nano Hydroxyapatite Coating and  
its Formation Mechanism**

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## 摘 要

HA/Ti 复合材料可以发挥 HA 和医用金属的综合优势。已发展了多种制备 HA/Ti 复合材料的技术, 各种方法均有优缺点。电化学沉积法是制备生物陶瓷膜层的一种新方法, 其优点是: 温和的沉积条件可避免 HA 晶相的破坏; 简单易控的沉积过程易于实现不同性能涂层的可控制备; 非线性的涂覆过程, 适合于外形复杂的金属基底材料。本文侧重发展电化学沉积法, 通过系统研究, 实现 HA 涂层表面形貌结构的可控制备, 并探索其结构和性能关系。此外, 还对控制条件下羟基磷灰石的电化学沉积机理进行讨论。主要进展和结果如下:

### 1. 羟基磷灰石涂层的电化学可控制备

发展和完善了从水溶液体系中直接制备结晶完美的纯 HA 涂层的电化学沉积技术。调节沉积体系温度和电解液的浓度, 得知当 $[\text{Ca}^{2+}] \leq 4.2 \times 10^{-4} \text{M}$ 时, HA 的电化学沉积必须在沉积温度不低于  $70^\circ\text{C}$  下才能发生。温度升高有利于涂层中 HA 纯度的提高, 尤其当沉积温度为  $100^\circ\text{C}$  时, 由于类水热处理条件的建立, 促进了其它晶型磷酸钙盐向 HA 的转化, 保证涂层为更纯的 HA。

XRD 和 FT-IR 表征结果表明, 所制备的涂层为结晶度较高的纯 HA; SEM 观察到电沉积的 HA 涂层呈现的三种代表性形貌结构, 主要有: 细针状、散花簇状和交联多孔状。细胞培养实验发现, 各种 HA 涂层的生物相容性均较好, 而生物活性随形貌不同有较大的差异。交联多孔状 HA 涂层的生物活性最好, 具有较强的引导细胞生长的能力。材料的生物相容性和生物活性主要取决于材料表面的形貌和结构特征。

同时, 还通过系统的改变沉积时间、电流密度、体系 pH 值和电解液浓度等电沉积参数, 全面考察了各实验参数对 HA 电沉积生长过程的影响, 摸索总结 HA 的电化学制备规律性, 基本实现三种典型形貌 HA 涂层的电

化学可控制备。

## 2. 羟基磷灰石的电化学沉积形成机理研究

对含有高低电解液浓度的两种体系中常见磷酸钙盐的活度积进行热力学计算，对照其溶度积，粗略分析了高低两种浓度体系下 HA 的电沉积生长过程机理。得知在低浓度体系，热力学上禁阻了前驱体的形成，有利于在电沉积过程中获得高纯的 HA。

在低浓度体系下，研究了不同沉积时间的 HA 涂层的红外漫反射光谱和拉曼光谱，了解 HA 电沉积初期的反应过程。结合热力学初步计算和实验研究结果，发展和完善了 HA 电沉积的两步法机理，提出二级结构模型，解释了电沉积过程三种代表性形貌特征的 HA 涂层的形成机理。

## 3. 纳米羟基磷灰石粉体材料的宏量制备

为了实现纳米 HA 的宏量制备，用化学共沉淀和水热后处理相结合的方法在实验室小试研究 HA 粉体的制备。通过调控反应物浓度和水热处理时间，实现了结晶度较高且晶粒尺寸在 20nm ~ 30nm 之间的纯 HA 粉体的宏量制备。

**关键词:** 羟基磷灰石涂层 电化学可控制备 生物性能 形成机理 宏量制备

## Abstract

Hydroxyapatite coatings can endow the surface metallic materials with a bioactivity, thus integrate the proper mechanical properties of the metal substrate with the excellent biological properties of the coating. Many techniques such as plasma spraying, electrophoresis, electrochemical deposition, sol-gel, biomimetic methods, etc. have been developed to prepare HA coatings on metallic substrates. Among them the electrochemical deposition method is one of the most flexible and versatile techniques. Electrochemical deposition method possess several advantages, including moderate deposition conditions that avoid high temperature destruction of the HA crystal phase, nonlinear coating procedure that fits for rough substrates, flexible deposition process which is readily to realize a controllable preparation.

In this work, the electrochemical deposition technique has been systematically studied in order to exploit a well-controlled method to prepare bionic bone coating, and the structure controllability has been emphasized as well. The hydroxyapatite coatings with different morphologies have been prepared, and the relationship between structure and properties of the prepared hydroxyapatite coatings has been studied. In addition, the electrochemical deposition mechanism of hydroxyapatite coatings in different systems has been discussed in the paper. The main conclusions are listed as follows:

### **1. Controllable Preparation of HA Coatings by Electrochemical Deposition Method**

By adjusting the deposition temperature and concentration of the electrolytes, the hydroxyapatite deposition reaction takes place at the temperature over 70°C, under the condition of  $[Ca^{2+}] \leq 4.2 \times 10^{-4} M$ . The purity of hydroxyapatite coatings can be improved with the increasing temperature, especially at 100°C. The results of XRD and FT-IR characterization show that



the coatings are pure hydroxyapatite with high crystallinity. Three kinds of typical morphology of hydroxyapatite coatings are observed by SEM, they are standing-up, flower and ordered porous structures. In vitro test shows that all HA coatings exhibit good biocompatibility, but their bioactivities vary greatly with the various surface morphologies, while only the HA coating with ordered porous structures present the best bioactivities and strong ability to induce the growth of cell. The biocompatibility and bioactivity of material depends on the morphology and structure of the material surface.

The effect of the deposition parameters including deposition time, current density, pH values and concentration of electrolytes, on the process of HA electrochemical deposition has been studied. The HA coatings with different morphologies and structures have prepared by the controllable electrochemical deposition.

## **2. Formation Mechanism of the HA Coatings by Electrochemical Deposition**

The activity products of different calcium phosphates in high-concentration system and low-concentration system are given by thermodynamic calculation, respectively. By contrast of their solution products, the basic mechanism of the HA growth in these two systems is analyzed. The results show that a highly pure HA can be obtained in the low-concentration system, where the formation of the precursor is forbidden by the thermodynamic consideration.

In the low-concentration system, the IR diffuse reflection and Raman spectroscopy are used to study the process of HA growth by electrochemical deposition by varying different preparing time. Combining thermodynamic calculations and experimental results, the two-step mechanism with two-order mode is proposed to explain the formation mechanism of HA coatings with three typical morphologies in low-concentration electrolyte system.

## **3. A Large-Scale Preparation of Nano-Hydroxyapatite Powders**

In order to realize a large scale preparation of nano powders of HA, the

combination of chemical co-precipitation and hydrothermal treatment is developed in the lab. By controlling the concentration of reactants and the time of hydrothermal treatment, pure HA powders with high crystallinity and the crystal size of 20~30nm have been successfully synthesized.

**Keywords:** Hydroxyapatite coating, Electrochemically controllable deposition, Bioproperty, Formation mechanism, A large-scale preparation

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## 目 录

<b>第一章 绪 论</b> .....	1
§ 1.1 生物材料简介 .....	1
§ 1.2 三大生物材料 .....	2
§1.2.1 医用金属材料 .....	2
§1.2.2 医用高分子材料 .....	4
§1.2.3 生物陶瓷材料 .....	4
§ 1.3 钛表面 HA 涂层的制备方法 .....	6
§1.3.1 等离子喷涂法 .....	7
§1.3.2 爆炸喷涂法 .....	8
§1.3.3 电泳沉积法 .....	8
§1.3.4 离子束溅射法 .....	8
§1.3.5 涂覆-烧结法 .....	8
§1.3.6 激光熔覆法 .....	8
§1.3.7 溶胶-凝胶法 .....	9
§1.3.8 仿生合成法 .....	9
§ 1.4 HA 涂层的电化学沉积法制备 .....	9
§ 1.5 本论文的研究目的和设想 .....	12
参考文献 .....	13
<b>第二章 实验方法和仪器</b> .....	17
§ 2.1 电化学沉积模式 .....	17
§ 2.2 X 射线衍射 .....	17
§ 2.3 红外光谱 .....	19
§ 2.4 拉曼光谱 .....	20

§ 2.5	扫描电子显微镜	20
§ 2.6	生物医用材料的生物学评价	21
§2.6.1	体外实验	21
§2.6.2	体外实验细胞的选择	21
§2.6.3	细胞培养	23
§2.6.4.1	细胞培养与诱导分化处理	23
§2.6.4.2	生物材料样品的准备和细胞培养	24
§2.6.4.3	扫描电镜实验用细胞样品的准备	24
	参考文献	26
<b>第三章 纳米 HA 涂层的电化学可控制备及其性能表征</b>		<b>27</b>
§ 3.1	羟基磷灰石涂层的电化学研究	27
§ 3.2	电解液的配制及电沉积条件	28
§3.2.1	电沉积实验装置	29
§3.2.2	电解液的配制	29
§3.2.3	电沉积羟基磷灰石膜层的实验条件	30
§ 3.3	结果与讨论	30
§3.3.1	电沉积钙磷盐涂层的结构表征	30
§3.3.2	电沉积钙磷盐涂层的组分表征	32
§3.3.3	电沉积钙磷盐涂层的形貌表征	33
§3.3.4	电沉积HA涂层的生物性能初步表征	35
§3.3.5	不同形貌HA涂层的电化学可控制备规律	37
§3.4	本章小结	38
	参考文献	39
<b>第四章 纳米羟基磷灰石涂层电沉积机理的研究</b>		<b>41</b>

§ 4.1	羟基磷灰石的电沉积机理研究	41
§ 4.2	羟基磷灰石膜层的电沉积制备	43
§4.2.1	电沉积条件	43
§3.2.1	电沉积模式	43
§ 4.3	结果与讨论	43
§4.3.1	羟基磷灰石涂层的电沉积制备规律	43
§4.3.1.1	沉积温度的影响	43
§4.3.1.2	电解液浓度的影响	45
§4.3.1.3	沉积时间的影响	46
§4.3.1.4	体系pH值的影响	48
§4.3.1.5	电流密度的影响	49
§4.3.1.6	HA涂层的电沉积制备规律总结	54
§4.3.2	羟基磷灰石的电沉积机理初步探讨	55
§4.3.2.1	HA电沉积过程的红外和拉曼研究	55
§4.3.3.2	相关的热力学计算和机理解释	56
§ 4.4	本章小结	63
	参考文献	64
 <b>第五章 纳米羟基磷灰石粉体的宏量制备</b>		 65
§5.1	引言	65
§5.1.1	羟基磷灰石简介	65
§5.1.2	羟基磷灰石粉体制备方法	65
§5.2	纳米HA粉体的小试制备研究	68
§5.2.1	纳米HA粉末颗粒尺寸控制条件	68
§5.2.2	共沉淀法制备HA的工艺流程图	69
§5.2.3	小试所得的HA粉末的表征及讨论	69

---

§5.2.3.1 粉末的XRD表征 .....	69
§5.2.3.2 粉末的FT-IR表征 .....	71
§5.2.3.3 粉末的TEM表征 .....	72
§5.2.3.4 HA粉体的小试研究总结 .....	73
<b>§5.3 纳米HA粉体的中试制备 .....</b>	<b>74</b>
§5.3.1 纳米HA粉体中试合成所用的仪器 .....	74
§5.3.2 中试合成的流程及操作注意事项 .....	74
§5.3.2.1 中试合成的工艺流程 .....	74
§5.3.2.2 中试操作过程中的注意事项 .....	75
§5.3.3 中试制备的纳米HA粉末的表征及结论 .....	75
<b>§5.4 本章小结 .....</b>	<b>76</b>
参考文献 .....	77
<b>第六章 主要结论和研究展望 .....</b>	<b>80</b>
§6.1 本论文的主要结论 .....	80
§6.2 拟进一步开展的研究工作 .....	81
作者攻读硕士学位期间发表与交流论文 .....	82
致 谢 .....	84

## Contents

<b>Chapter 1. Introduction</b> .....	1
<b>§1.1 Brief Introduction of Biomaterials</b> .....	1
<b>§1.2 Three kinds of Biomedical Materials</b> .....	2
§1.2.1 Biomedical metal Materials .....	2
§1.2.2 Biomedical Macromolecule Materilas .....	4
§1.2.3 Bioceramics Materials .....	4
<b>§1.3 Methods of Hydroxyapatite Coatings on Titanium Substrate</b> .....	6
§1.3.1 Plasma Sprayed Method .....	7
§1.3.2 Explosion Sprayed Method .....	8
§1.3.3 Electrophoresis Deposition .....	8
§1.3.4 Ion Beam Spattering Method .....	8
§1.3.5 Coat-sintered Method .....	8
§1.3.6 Laser Cladding Method .....	8
§1.3.7 Sol-Gel Method .....	9
§1.3.8 Biomimetic Synthesis .....	9
<b>§1.4 Electrochemical Preparation of HA coatings</b> .....	9
<b>§1.5 Objective and Contents of this Dissertation</b> .....	12
References .....	13
<b>Chapter 2. Experimental Methods and Instruments</b> .....	17
<b>§2.1 Mode of Electrochemical deposition</b> .....	17
<b>§2.2 X-ray Diffraction Method</b> .....	17
<b>§2.3 Infrared Spectroscopy</b> .....	19
<b>§2.4 Raman Spectroscopy</b> .....	20



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