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·综述·

锶离子改性钛种植体表面研究进展

姜小维[1]，　石安源[1]，　郭丽[1]，　顾春宁[1]，　秦海燕[2]
1. 南京大学医学院附属口腔医院，南京市口腔医院种植科，江苏　南京（210008）；　2. 南京大学医学院附属鼓楼医院，南京鼓楼医院口腔科，江苏　南京（210008）

【摘要】 传统钛种植体缺乏生物活性，不能完全满足临床要求。锶离子对钛种植体表面改性可以增强其骨结合能力，减少种植体周围炎的发生。本文就锶离子改性钛种植体表面的生物性能进行综述。目前研究表明，锶离子可以通过水热处理、电化学沉积、磷酸盐化学转化、火焰喷涂、超分子自组装、磁控溅射、激光沉积和碱腐蚀等方法添加到种植体表面。锶离子改性的钛种植体表面能促进成骨、增强早期骨结合、抑制细菌生长、减少术后感染；当锶离子与其他元素如银、锌、镓、钙等掺杂时，具有更好的骨结合和抗菌效果。但关于锶离子改性钛种植体表面的研究大多为动物实验和体外实验，观察时间与种植体实际使用寿命相比较短，所得结论可能与实际临床应用有所差别，长期效果有待研究；此外，各种改性方法之间的成骨效果也需要进一步比较。未来的研究可以关注以下几点：①寻找高效的，可以广泛临床应用的改性方法；②研究如何控制种植体附近的锶离子浓度，在发挥其生物学功能的同时，减少毒副作用；③进行长期随访的临床实验以观察其成骨及抗菌效果。

【关键词】 锶离子；　钛；　种植体；　成骨性能；　表面改性；　抗菌性能；　银离子；　锌离子；　水热处理；　电化学沉积

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Research progress on surface modification of titanium implants by strontium ions

JIANG Xiaowei[1], SHI Anyuan[1], GUO Li[1], GU Chunning[1], QIN Haiyan[2]. 1. Department of Dental Implantology, Nanjing Stomatological Hospital, Medical School, Nanjing University, Nanjing 210008, China; 2. Department of Stomatology, Affiliated Drum Tower Hospital, Medical School, Nanjing University, Nanjing 210008, China
Corresponding author: QIN Haiyan, Email: haiyanandrew@163.com, Tel: 86-25-83106666-55303

【Abstract】 Traditional titanium implants do not completely meet the clinical requirements because they are bioinert. The surface of titanium implants, modified by strontium ions, can enhance osseointegration and reduce peri-implantitis. In this paper, the biological properties of titanium implant surfaces modified by strontium ions were reviewed. Strontium ions can be coated on the implant surface by hydrothermal treatment, electrochemical deposition, phosphate chemical conversion, flame-spraying, supramolecular self-assembly, magnetron sputtering, laser deposition and alkali etching. Implant surfaces modified by strontium ions can not only promote osteogenesis and early osseointegration but also inhibit bacterial growth and reduce postoperative infections. Even better osseointegration and antibacterial effects can be achieved when strontium ions are incorporated with other elements, such as silver, zinc, gallium, and calcium. However, most of the studies on the use of strontium ion-modified titanium implants are animal experiments and *in vitro* experiments, and the observation time is short compared with the actual service life of the implants. Thus, the conclusions obtained may be different from the actual clinical application, and the long-term effects need to be studied. In addition, the osteogenic effects of various modification methods also need to be compared. Future research can focus on the fol-

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【作者简介】 姜小维，医师，硕士，Email: 2193578729@qq.com
【通信作者】 秦海燕，副主任医师，博士，Email: haiyanandrew@163.com，Tel: 86-25-83106666-55303

lowing points: ① to find efficient modification methods that can be widely used in the clinic; ②to study how to control the concentration of strontium ions near the implant to exert their biological function and reduce their toxic side effects; and ③ to conduct long-term follow-up clinical trials to observe their osteogenic and antibacterial effects.

【Key words】 strontium ions; titanium; dental implants; osseointegration; surface modification; antibacterial property; silver ions; zinc ion; hydrothermal treatment; electrochemical deposition

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纯钛及钛合金因密度小、弹性模量低、强度高、生物相容性好、耐腐蚀等优点被广泛应用于牙科种植体[1]。但传统的钛种植体因生物活性低、易引起种植体周围感染等因素，难以满足目前临床需求[2]。近年来，锶离子改性受到研究者的广泛关注。研究表明，锶离子不仅在促进成骨细胞增殖的同时抑制破骨细胞分化[3]，还具有杀菌和抑菌的潜能[4]。因此，锶离子改性钛种植体在改善骨整合和减少种植体感染方面具有重要的临床价值。本文就锶离子改性钛种植体表面的相关研究进行综述。

1　锶离子改性钛种植体表面的应用技术

1.1　水热处理

水热处理是将钛浸没在含有目的元素的溶液中，在一定压力下加热一段时间，即可在钛表面形成含有该元素的纳米涂层的方法[5]。通过改变溶液的成分，改变涂层的组成[6]；改变溶液的浓度、温度、处理的压力和时间，可以在原本光滑的钛表面形成纳米花瓣状、纳米网格状或更大孔径相互连通的三维多孔片状结构[7]。与其他方法相比，水热处理更加简单、经济和有效。此外，该方法可与其他表面处理方法联合使用，如在水热处理后焙烧，可以提高镓-锶层状双氢氧化物复合涂层、pH，提高该涂层的抗菌能力[8]。

1.2　电化学沉积

电化学沉积法是将材料置于相应的微量元素溶液或熔盐中，通过放电使位于阴极的材料表面镀上金属薄膜的技术[9]。电镜下可见钛表面形成带状或花朵状晶体结构。其优点是通过改变温度、电解液浓度和pH等因素控制涂层的性能[10]。等离子体电解氧化(plasma electrolytic oxidation，PEO)，也被称为微弧氧化(micro-arc oxidation，MAO)，是一种电化学沉积法，指在等离子体放电的辅助下，在金属表面形成一层厚且稳定的氧化物涂层[11]。和其他电化学沉积技术相比，PEO具有一步工艺的优势，成本相对较低，更易于控制[12]。

1.3　磷酸盐化学转化

磷酸盐化学转化法(phosphate chemical conversion，PCC)是一种将金属样品浸入设计好的磷化液中，通过化学反应在金属表面制备无机涂层的技术[13]。PCC具有成本低、操作简单、重复性高、对基质金属的力学性能影响小等独特优势，适用于不规则和结构复杂的表面[14]。制备的锶涂层通常具有较高的结晶度和稳定性，不仅能为钛衬底提供良好的保护屏障，还可以减缓涂层降解和离子释放速率[15]。

1.4　其他

火焰喷涂法是利用可燃气体与高压氧气在燃烧中产生高温高压焰流，熔化粉末、线材或棒状的材料并喷射至基体形成涂层的一种方法[16]。超分子自组装法是利用分子间的非共价键在材料表面自发生成纳米薄膜[17]。磁控溅射法是利用带电粒子轰击靶材，溅射出靶材表面粒子，使其沉积在基底表面形成纳米涂层结构[18]。激光沉积是通过激光与靶材相互作用，产生的等离子体膨胀后沉积在基底上形成涂层[19]。碱腐蚀法只需在室温下将钛浸泡在含有相应的微量元素的碱性溶液中，即可制备含有目的元素的纳米线状涂层，涂层的形成是一个溶解-再结晶过程[20]。

采用上述方法将锶离子附着到钛种植体表面时，既要考虑结合材料的特征，又要考虑各种方法的效率、费用等因素，并且各种方法之间的成骨效果也需要进一步比较研究。

2　锶离子单独或与其他元素联用对种植体表面的改性

单纯改变钛种植体表面形态对其生物活性提

升有限，和微量元素改性结合，可以在此基础上赋予钛种植体不具备的生物功能[21]。锶离子改性不仅能促进成骨，还能抑制细菌。并且当锶离子与其他元素联合使用时，成骨和抑菌效果可以得到进一步提高。

2.1　锶

锶是人体骨形成所必需的元素，可以通过丝裂原活化蛋白激酶/细胞外调节蛋白激酶（motigen-activated proteinkinase/extracelluar regulated protein kinase，MAPK/ERK）、环氧化酶2/前列腺素E2（cyclooxygenase-2/Prostaglandin E2，COX-2/PGE2）、钙调神经磷酸酶/活化T细胞核因子（calcineurin/nuclear factor of activated T cells，Calcineurin/NFATc1）、Wnt和蛋白激酶B（protein kinase B，Akt）等多种途径发挥作用，促进成骨细胞增殖，抑制破骨细胞分化[22-23]。Wang等[21]采用磁控溅射法制备的纳米级钛酸锶涂层可促进成骨基因如碱性磷酸酶（alkaline phosphatase，ALP）、Runt相关转录因子2（runt-related transcription factor 2，Runx2）、骨钙素（osteocalcin，OCN）、骨桥蛋白（osteopontin，OPN）和Ⅰ型胶原蛋白（collagen typeⅠ，COL-1)的表达，抑制破骨细胞基因细胞核因子κB受体活化因子配体（receptor activator of NF-κB ligand，RANKL）和抗酒石酸酸性磷酸酶（tartrate-resistant acid phosphatase，TRAP）表达，从而促进成骨，抑制骨吸收。锶离子可通过募集骨髓间充质干细胞（bone marrow mesenchymal stem cells，BMSCs）发挥作用[24]。Zhou等[25]通过水热处理制备的掺锶微/纳米钛涂层植体触发了野生型大鼠体内被标记的BMSCs向植入部位募集。骨组织的血管化[26]和巨噬细胞的抗炎表型M2分化[27]都能促进骨整合。Lu等[28]采用水热处理制备的掺锶微/纳米钛涂层在体外实验中促进了血管生成和巨噬细胞M2型分化，在体内实验中，增加了大鼠胫骨种植体模型中H型血管的形成，促进了早期血管化骨整合。锶离子功能化表面具有抗菌潜力，可以减少由细菌引起的种植体周围炎所导致的种植失败[29-30]。Praharaj等[31]采用阳极氧化技术制备的载锶二氧化钛纳米棒对大肠杆菌和金黄色葡萄球菌具有良好的抗菌活性。自噬在骨骼动态平衡中起着至关重要的作用[32]。Wang等[33]采用水热处理技术制备的掺锶微/纳米钛涂层可在上调BMSCs自噬和分化的同时下调破骨细胞自噬和分化，从而显著促进种植体的骨结合。

传统钛种植体在骨质疏松症和糖尿病等系统性疾病患者中的种植效果并不理想[34]。Liu等[35]通过磁控溅射法制备了载锶米/纳米钛涂层种植体，在绵羊骨质疏松模型中具有更好的骨结合能力，表明具有该涂层的种植体有望用于骨质疏松患者。Lin等[5]采用水热处理在钛种植体表面添加锶，发现该种植体可能通过Wnt5a信号途径促进糖尿病大鼠的骨整合。

种植体表面的磷灰石形成能力与骨整合呈正相关[36]。Geng等[37]采用碱热处理制备了含锶钛种植体，锶含量的增加虽然能促进BMSCs的增殖和成骨分化，但降低了种植体表面形成磷灰石的能力，所以笔者认为需要优化锶含量以平衡磷灰石形成能力和成骨活性，实现理想的骨整合。锶离子的实际有效浓度因植入材料的不同而不同，如Yan等[12]制备的锶锌涂层的有效锶离子浓度0.2～5.0 mmol/L。目前已有量化锶在种植体周围骨组织分布的研究[38]。

以上研究表明，锶离子可以提高种植体骨结合和抑菌能力，在骨质疏松和糖尿病模型中也能取得良好的效果。但仍需进一步研究如何优化种植体周围锶离子的浓度，以实现理想骨整合。

2.2　锶和银

银是一种广谱抗菌剂，其改性的种植体具有出色的抗菌抗炎能力。但当浓度超过一定阈值时，对人体细胞有一定的毒性[39]。Geng等[40]研究表明锶的共取代可以减轻银的不利影响，提高细胞的活力。Okuzu等[41]采用改良的碱热处理在钛表面制备了含锶和银的涂层，不仅促进了早期骨结合，而且显著提高了抗菌活性，对金黄色葡萄球菌和大肠杆菌的抗菌率超过95%。而且早期成骨分化相关基因的表达水平也高于对照组，作者认为这可能与锶和银之间的电偶作用有关。Li等[42]构建了锶离子和银离子双传递体系，这种程序化递送系统通过调控巨噬细胞的极化来清除病原体，并激活成骨前细胞分化，显示出锶和银协同促进组织愈合、抗菌和成骨特性。

2.3　锶和锌

锌是人体内重要的微量元素，对种植体周围炎相关细菌起到抑制作用[43]，锌和锶离子可提高成骨细胞分化和矿化相关基因ALP、Runx2和Col-1的表达水平[37]。Chen等[44]采用水热处理在钛表面制备了锌锶共掺涂层，结果表明该涂层可促进BMSCs黏附、增殖和成骨分化。Zhao等[45]采用微弧氧化技术在钛表面制备了含锌、锶的微孔涂层，抗菌

试验表明，该涂层抑制葡萄球菌的增殖，具有良好的抗菌活性，说明锌离子首先与细菌的细胞壁相互作用，随后使细菌细胞膜结构发生改变，同时可能损害了细菌DNA，最终导致细胞死亡。

2.4　锶和镓

镓具有抑制破骨细胞性骨吸收、促进骨形成的能力。Chen等[46]采用水热处理方法在钛表面制备了锶镓涂层，该涂层不仅对间充质干细胞（mesenchymal stem cells，MSCs）具有良好的细胞相容性，还能有效提高MSCs的自噬水平，促进MSCs的成骨分化。镓离子可抑制金黄色葡萄球菌和铜绿假单胞菌的活性[47]。Li等[8]采用水热处理将镓和锶离子改性到钛衬底上，抑菌实验表明，镓离子可以破坏细菌的铁代谢，产生活性氧，从而使该涂层获得很强的抗菌能力。

2.5　锶和其他元素

Zhang等[48]在钛表面制备了锶钙共掺杂涂层。与对照组相比，该组细胞外基质矿化的速度更快，表明锶钙共掺杂涂层具有更强的骨形成能力。Zhou等[2]采用锶、钡改性钛种植体，结果表明，在锶离子释放的协同作用下，该涂层改善了大鼠BMSCs的早期黏附和成骨分化，显著提高钛种植体的骨整合能力。硅可以增强成骨细胞黏附、增殖、分化和骨整合能力[49]。Qiao等[50]使用电化学沉积法制备了硅、锶、银共掺杂涂层，锶和硅的掺杂提高了成骨相关基因的表达水平，并抵消了银离子的潜在细胞毒性。

3　小　结

综上所述，锶离子可通过水热处理、电化学沉积、PCC等方法改性到钛种植体表面，提高种植体骨整合和抑菌能力，提高种植手术的成功率。当锶离子与其他元素如银、锌、镓、钙等掺杂时，甚至会有更好的效果。因此，锶离子改性的钛种植体具有良好的应用前景。目前，关于锶离子改性钛种植体表面的研究大多为动物实验和体外实验，观察时间与种植体实际使用寿命相比较短，所得结论可能与实际临床应用有所差别，长期效果有待研究。此外，各种改性方法之间的成骨效果也需要进一步比较。未来的研究可以关注以下几点：①寻找高效的，可以广泛临床应用的改性方法；②研究如何控制种植体附近的锶离子浓度，在发挥其生物学功能的同时，减少毒副作用；③进行长期随访的临床试验以观察其成骨及抗菌效果。

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（编辑　罗燕鸿）

官网

· 短讯 ·

《口腔疾病防治》入选2022年度中国高校科技期刊建设示范案例库优秀科技期刊

2022年12月1日，在中国高校科技期刊研究会第26次年会上发布了2022年度中国高校科技期刊建设示范案例库·杰出/百佳/优秀科技期刊入库案例名单。由南方医科大学口腔医院主办的科技期刊《口腔疾病防治》入选2022年度中国高校科技期刊建设示范案例库优秀科技期刊。

《口腔疾病防治》编辑部