

Strontium and Zinc doped hydroxyapatite coating on stainless steel mini-implants used in maxillofacial surgery: An in-vitro study

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ABSTRACT

Aims: This study aims to achieve an electrochemical deposition of Sr- and Zn-doped hydroxyapatite coating on stainless steel mini-implants and verify it by Fourier transform infrared spectroscopy (FTIR). **Materials and methods:** Synthesis of the powder: Zinc-Sr hydroxyapatite nanoparticles were synthesised in this work using a sonochemical-mediated hydrothermal technique. **Electrochemical deposition of the coating:** The coating was applied electrochemically onto commercially available stainless steel miniplates measuring 2 mm in thickness and screws measuring 2 x 8 mm. The coated implants were analysed for their functional groups using Fourier transform infrared spectroscopy (FTIR) covering a frequency range of 4000–400 cm⁻¹. **Results:** The chemical nature and functional groups involved in the successful production of Zn-Sr/HAP were predominantly elucidated by FT-IR spectroscopy investigations. In FTIR, the coated stainless-steel plates showed 3 peaks at 1024.85, 601.02, and 561.26. The coated stainless-steel screws showed 2 peaks at 1028.43 and 563.23. **Conclusion:** Zinc and strontium-doped hydroxyapatite coating can be done on stainless steel miniplates using electrochemical deposition.

Keywords: Strontium and Zinc doped hydroxyapatite coating, stainless steel mini-implants, in-vitro study

INTRODUCTION

AO (Arbeitsgemeinschaft für Osteosynthesefragen) established internal fixation by plating for maxillofacial traumas as the primary method of fixation. Miniplates were introduced in 1973 by Michelete, and later Champy in 1975 gave the ideal line of osteosynthesis by monocortical screw fixation [1]. Since then, miniplates have replaced other fixation techniques as the industry standard in maxillofacial surgery. In an attempt to enhance the qualities of these miniplates, manufacturers have experimented with different lot metals and their alloys [2]. Stainless steel, titanium, cobalt chrome, magnesium, tantalum, zinc, and their alloys have been used. Among these implants, titanium implants have been most sought after because they have superior mechanical properties, are bioinert, and undergo osseointegration with the host bone [3]. Despite stainless steel being inferior to titanium, it is still used to this day because titanium is more expensive and cannot be afforded by most patients in developing countries [4].

This study aims to achieve an electrochemical deposition of Sr- and Zn-doped hydroxyapatite coating on stainless steel mini implants and verify it by Fourier transform infrared spectroscopy (FTIR).

Materials and Methods:

Synthesis of the powder:

Zinc-Sr hydroxyapatite nanoparticles were synthesised in this work using a sonochemical-mediated hydrothermal technique. The synthesis procedure involved adding 50 mL of a 1 M solution of Strontium Nitrate, 0.5 M Zinc Nitrate Hexahydrate, and 0.6 M $\text{NH}_4\text{H}_2\text{PO}_4$ drop by drop (at a rate of 0.5 mL per minute) while continuously stirring using a magnetic stirrer (MS 500 series, REMI, India). The phosphate and selenite mixed solution should be added drop by drop to the calcium salt and dispersion agent mixed solution, and allowed to react for 1.5-2.5 hours. The pH of the resulting solution was regulated within the range of 10–10.5 by the addition of liquid ammonia. Prior to thorough mixing, the suspension underwent ultrasonic treatment in an ultrasonic bath for a duration of 10 minutes [5]. Next, the prepared suspension was moved to an autoclave and subjected to hydrothermal treatment at 180°C for 10 hours. The precipitate obtained was filtered and carefully rinsed with deionised water many times to eliminate any undesired inorganic remains. The washing process was continued until all organic residues were eliminated, therefore protecting against agglomeration. Subsequently, the precipitate underwent multiple ethanol washes and was naturally dried at ambient temperature. In addition, the samples designated for additional analysis were dehydrated in a hot air oven set at 100°C for 21 hours. The last precipitate was pulverised into fine particles using a mortar and pestle set [6].

Electrochemical deposition of the coating:

The coating was applied electrochemically onto commercially available stainless steel miniplates measuring 2 mm in thickness and screws measuring 2 x 8 mm. Following surface treatment on silicon carbide paper, both samples were degreased with isopropyl alcohol and then cleaned in acetone for 30 minutes in an ultrasonic bath. The electrochemical deposition (ED) was conducted in a three-electrode cell utilising a galvanostatic pulse protocol. The preparation of the electrolyte for hydroxyapatite-based coatings involved the dissolution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, ZnCl_2 , and $\text{Sr}(\text{NO}_3)_2$ salts in water. Within this procedure, the stainless steel substrate served as the working electrode (WE), the saturated calomel electrode (SCE) acted as the reference electrode (RE), and the platinum sheet formed the auxiliary electrode (AE). The galvanostat PARSTAT MC (Princeton Applied Research-AMETEK, Berwyn, PA, USA) was employed to deposit the coating [7].



Figure 1: Coated stainless steel plate



Figure 2: Coated stainless steel screws

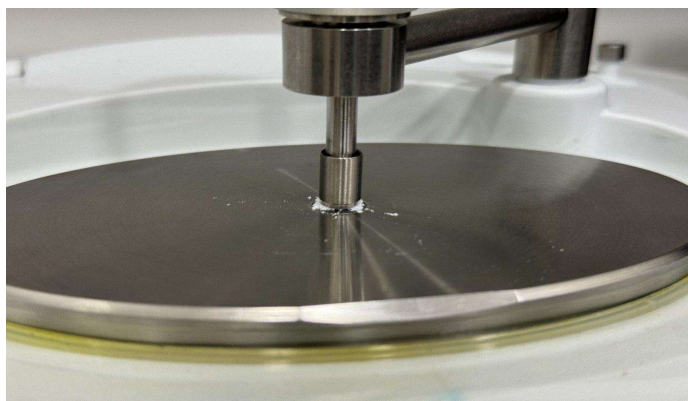


Figure 3: FTIR analysis of Zn-Sr-HAP powder

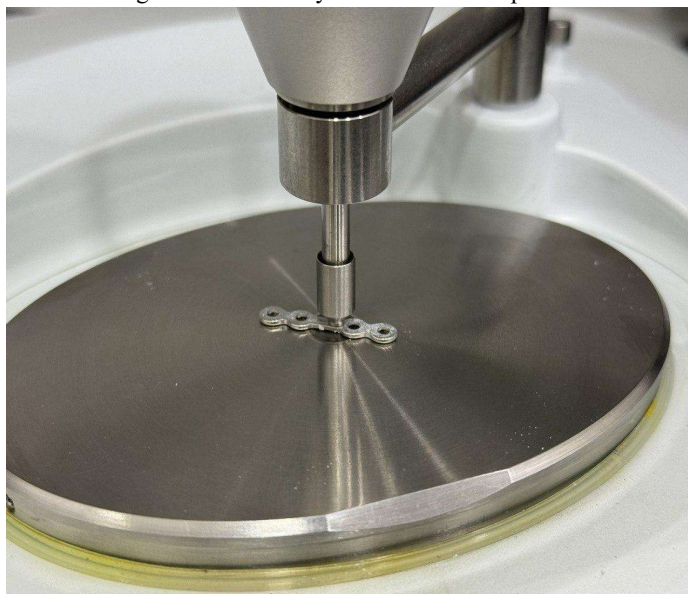


Figure 4: FTIR analysis of Coated plate

The coated implants were analysed for their functional groups using Fourier transform infrared spectroscopy (FTIR) covering a frequency range of 4000–400 cm^{-1} (ALPHA 2, Bruker Corporation, Billerica, USA).

Results:

The chemical nature and functional groups involved in the successful production of Zn-Sr/HAP were predominantly elucidated by FT-IR spectroscopy investigations, as depicted in Figure 1. The spectral peaks observed at around 563 cm^{-1} and 601 cm^{-1} correspond to the distinctive bending vibrations associated with P–O bonding in PO_4^{3-} . Furthermore, the stretching vibrations detected among the frequency range of 1000 cm^{-1} to 1100 cm^{-1} were identified as being linked to the stretching modes of the phosphate group in hydroxyapatite. Furthermore, a distinct peak detected at around 1450 cm^{-1} – 1470 cm^{-1} in the Sr-HAP spectrum confirms the existence of the CO_3^{2-} group in the Zn-Sr-HAP spectrum. The peak at around 3339 cm^{-1} corresponds to the OH-anion.

In FTIR, the coated stainless steel plates showed 3 peaks at 1024.85, 601.02, and 561.26 (Figure 6 & Table 2). The coated stainless steel screws showed 2 peaks at 1028.43 and 563.23 (Figure 7 & Table 3).

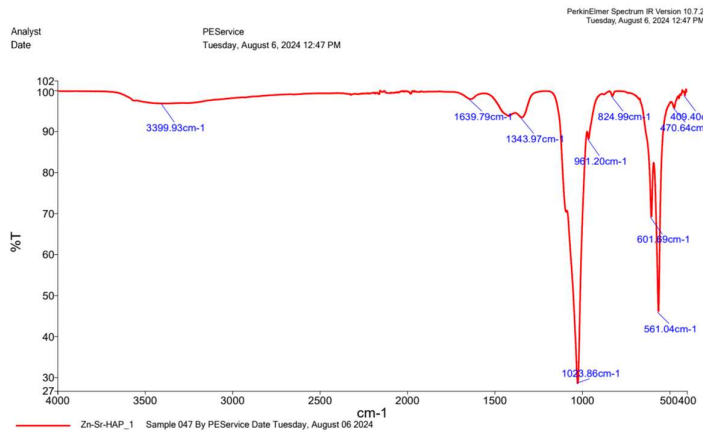


Figure 5: FTIR analysis of synthesised powder.

Peak number	X (cm-1)	Y(%T)
1	3399.93	97.00
2	1639.79	98.09
3	1343.97	93.60
4	1023.86	28.50
5	961.20	88.37
6	824.99	98.80
7	601.69	69.26
8	561.04	46.14
9	470.64	95.90
10	409.40	98.95

Table 1: Number of peaks observed in FTIR for Zn-Sr-HAP

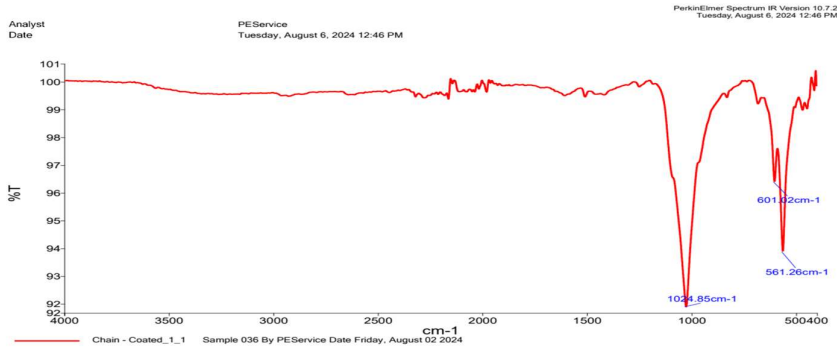


Figure 6: FTIR analysis of coated plate

Peak number	X (cm-1)	Y(%T)
1	1024.85	91.89

2	601.02	96.43
3	561.26	93.91

Table 2: Number of peaks observed in FTIR for coated plate

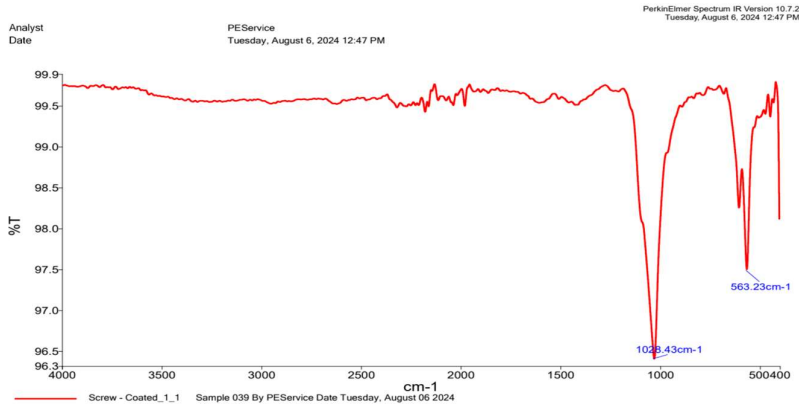


Figure 7: FTIR analysis of coated screw

Peak number	X (cm-1)	Y(%T)
1	1028.43	96.40
2	563.23	97.50

Table 3: Number of peaks observed in FTIR for coated plate

Discussion:

Fourier transform infrared (FTIR) spectroscopy can detect and measure chemical substances by their infrared absorption. The basic idea of FTIR spectroscopy is that molecules absorb infrared light at their vibrational frequencies. In a sample, chemical bonds absorb infrared light at specific frequencies, creating a molecular fingerprint spectrum [8]. Typically, the spectrum is displayed as absorbance versus wavenumber, measured in inverse centimetres (cm⁻¹). Fourier transform infrared (FTIR) spectroscopy has great utility in many disciplines. Chemically, it is employed for the purpose of identifying functional groups in organic molecules and investigating molecular conformations. It facilitates chemists in comprehending the makeup of intricate mixes and tracking chemical processes in real-time. It is used in materials science to examine polymers, composites, and coatings. This phenomenon offers a valuable understanding of material characteristics and can be employed to evaluate the quality of materials by identifying impurities or byproducts of deterioration [9].

Zinc (Zn) is a trace element that is indispensable to the human body and has a stimulating effect on bone metabolism. The proliferation, adhesion, and differentiation of osteoblasts can be improved by ZnO. The osteoblast cells exhibit an increase in alkaline phosphate activity as the percentage of ZnO increases [10]. Scanning electron microscopy (SEM) analysis of uncoated and coated glass slides revealed decreased bacterial colonies in ZnO-coated substrates compared to uncoated substrates. ZnO-coated substrates showed increased time-dependent antibacterial activity when submerged in suspension of *S. aureus* [11].

Strontium (Sr) ions have similar effects on the body, like calcium having bone seaking properties. Sr coatings on implants show enhanced cell adhesion, and the release of Sr from the implant surface can increase mesenchymal stem cell differentiation to osteoblast [12]. The coating of Sr layer on stainless steel can enhance cell adhesion, enhance biocompatibility, and enhance osseointegration. While Zn can improve the antibacterial activity of stainless steel implants, thereby bridging the gap between the properties of titanium and stainless steel. The zinc coatings emit zinc ions into the immediate surroundings. These ions undermine the integrity of the microbial cell membrane and disturb several bacterial processes, such as enzyme activity and nutrient absorption [13]. Microbial biofilms frequently develop on the surfaces of implants, therefore giving rise to chronic illnesses. The presence of zinc ions can impede the early bacterial attachment and the development of biofilms, therefore significantly

decreasing the likelihood of such infections. Zinc produces reactive oxygen species (ROS) that can cause oxidative stress, resulting in the destruction of bacterial DNA and proteins and ultimately cell death [14]. This method exhibits high efficacy against a diverse array of aggressive bacteria. Strontium enhances both bone density and the intrinsic structural integrity of the bone. A consequence of this is the development of a more robust and durable bone matrix surrounding the implant, therefore improving its overall integration and functionality [15].

Conclusion:

Zinc and strontium-doped hydroxyapatite coating can be done on stainless steel miniplates using electrochemical deposition.

Limitations of the study:

Further research on zinc and strontium coating to test the antimicrobial properties, cell adhesion, and osseointegration by animals is essential.

Conflict of interest:

This study did not receive any funding.

References:

1. Gotman, I. 1997. "Characteristics of Metals Used in Implants." *Journal of Endourology* 11 (6): 383–89.
2. Luhr, H. G. 2000. "The development of modern osteosynthesis." *Mund-, Kiefer- und Gesichtschirurgie: MKG* 4 Suppl 1 (May):S84–90.
3. Memarzadeh, Kaveh, Amir S. Sharili, Jie Huang, Simon C. F. Rawlinson, and Robert P. Allaker. 2015. "Nanoparticulate Zinc Oxide as a Coating Material for Orthopedic and Dental Implants." *Journal of Biomedical Materials Research Part A* 103 (3): 981–89.
4. Tao, Zhou-Shan, Wan-Shu Zhou, Xing-Wen He, Wei Liu, Bing-Li Bai, Qiang Zhou, Zheng-Liang Huang, et al. 2016. "A Comparative Study of Zinc, Magnesium, Strontium-Incorporated Hydroxyapatite-Coated Titanium Implants for Osseointegration of Osteopenic Rats." *Materials Science & Engineering. C, Materials for Biological Applications* 62 (May):226–32.
5. Popa, A., Fernandes, H., Neculescu, M., Luculescu, C., Cioangher, M., Dumitru, V., Stuart, B., Grant, D., Ferreira, J., & Stan, G. (2019). Antibacterial efficiency of alkali-free bio-glasses incorporating ZnO and/or SrO as therapeutic agents. *Ceramics International*, 45(4), 4368–4380. <https://doi.org/10.1016/j.ceramint.2018.11.112>
6. Y. Li, G. Feng, Y. Gao, E. Luo, X. Liu, J. Hu, Strontium ranelate treatment enhances hydroxyapatite-coated titanium screws fixation in osteoporotic rats, *J. Orthop. Res.* 28 (5) (2010) 578–582, <http://dx.doi.org/10.1002/jor.21050>.
7. P. Ammann, I. Badoud, S. Barraud, R. Dayer, R. Rizzoli, Strontium ranelate treatment improves trabecular and cortical intrinsic bone tissue quality, a determinant of bone strength, *J. Bone Miner. Res.* 22 (9) (2007) 1419–1425, <http://dx.doi.org/10.1359/jbmr.070607>.
8. P.J. Marie, Strontium ranelate: a dual mode of action rebalancing bone turnover in favour of bone formation, *Curr. Opin. Rheumatol.* 18 (Suppl. 1) (2006) S11–S15, <http://dx.doi.org/10.1097/01.bor.0000229522.89546.7b>.
9. S. Choudhary, P. Halbout, C. Alander, L. Raisz, C. Pilbeam, Strontium ranelate promotes osteoblastic differentiation and mineralization of murine bone marrow stromal cells: involvement of prostaglandins, *J. Bone Miner. Res.* 22 (7) (2007) 1002–1010, <http://dx.doi.org/10.1359/jbmr.070321>.
10. E. Bonnelye, A. Chabadel, F. Saltel, P. Jurdic, Dual effect of strontium ranelate: stimulation of osteoblast differentiation and inhibition of osteoclast formation and resorption in vitro, *Bone* 42 (1) (2008) 129–138, <http://dx.doi.org/10.1016/j.bone.2007.08.043>.
11. C.T. Wu, Y. Ramaswamy, D. Kwik, H. Zreiqat, The effect of strontium incorporation into CaSiO₃ ceramics on their physical and biological properties, *Biomaterials* 28 (21) (2007) 3171–3181, <http://dx.doi.org/10.1016/j.biomaterials.2007.04.002>.
12. F. Yang, W.J. Dong, F.M. He, X.X. Wang, S.F. Zhao, G.L. Yang, Osteoblast response to porous titanium

- surfaces coated with zinc-substituted hydroxyapatite, *Oral Surg. Oral Med. Oral Pathol. Oral Radiol.* 113 (3) (2012) 313–318, <http://dx.doi.org/10.1016/j.tripleo.2011.02.049>.
13. S.F. Zhao, W.J. Dong, Q.H. Jiang, F.M. He, X.X. Wang, G.L. Yang, Effects of zincsubstituted nano-hydroxyapatite coatings on bone integration with implant surfaces, *J. Zhejiang Univ. Sci. B* 14 (6) (2013) 518–525, <http://dx.doi.org/10.1631/jzus.B1200327>.
 14. Y. Li, Q. Li, S. Zhu, E. Luo, J. Li, G. Feng, Y. Liao, J. Hu, The effect of strontiumsubstituted hydroxyapatite coating on implant fixation in ovariectomized rats, *Biomaterials* 31 (34) (2010) 9006–9014, <http://dx.doi.org/10.1016/j.biomaterials.2010.07.112>.
 15. D. Hatakeyama, O. Kozawa, T. Otsuka, T. Shibata, T. Uematsu, Zinc suppresses IL-6 synthesis by prostaglandin F₂alpha in osteoblasts: inhibition of phospholipase C and phospholipase D, *J. Cell. Biochem.* 85 (3) (2002) 621–628, <http://dx.doi.org/10.1002/jcb.10166>.