

# Exploring the impact of hydroxyapatite coatings on zirconia dental implants: A short review

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## Abstract

Zirconia biomaterials have been used in dentistry for replacing missing teeth due to their superior biocompatibility, high mechanical properties, and higher corrosion resistance. These implant materials have a high modulus of elasticity, high stability, and great optical properties for aesthetic purposes. Nevertheless, the higher elastic modulus results in stress shielding effect of the hard tissue, leading to local bone resorption around the dental implant.

Various subtractive techniques have been used in the past two decades to modify the implant surface for better integration with the hard and soft tissue. With very limited additive techniques and few drawbacks, surface coatings are hardly being used over zirconia implants to improve the performance.

Hydroxyapatite (HA) is one of the ceramic biomaterials considered as an ideal material for coating on biomaterials as it possesses very close similarity in chemical composition and better biocompatibility with natural bone. Recently, the hydroxyapatite coating has increasingly drawn attention to improve the stability and adhesion quality of zirconia biomaterials. This short review presents the current progress in the adhesion qualities of hydroxyapatite coatings on zirconia biomaterials. The structural implant surface and microstructure of hydroxyapatite-based coating are also reviewed in this paper. Hydroxyapatite coated zirconia dental implant has a great potential for better integration with tissue. However, hydroxyapatite has certain drawbacks, including fracture toughness, brittle nature and lower tensile strength, which if overcome could be the promising additive surface coating for zirconia dental implants.

**Keywords:** ceramic implant surface, hydroxyapatite coating, osseointegration, zirconia implant

## Introduction

Zirconia is a bio-inert ceramic which doesn't react with living tissues nor cause any allergy or immune reactions. Particularly, an yttria-stabilised zirconia (YTZP) demonstrates excellent flexural strength and fracture resistance. Due to its superior mechanical and aesthetic properties, zirconia has been used in dentistry for decades for crowns and bridges. Also, from the past two decades, it has been used successfully to produce zirconia dental implants.<sup>1,2</sup> However, to achieve superior osseointegration zirconia is difficult to treat for surface modifications due to its hardness. Accordingly, many studies to overcome these problems through surface modification have been actively conducted in recent years.<sup>3</sup>

There are different surface modification techniques that have been applied to zirconia such as sand-blasting, acid etching, polishing, bio-functionalisation, laser treatment, coating, and ultraviolet light treatment. The purpose of surface modification is to alter the surface properties to enhance the biological performance of the surface, without changing the bulk properties of the material.<sup>3-5</sup>

Yttrium-stabilised zirconia reinforced hydroxyapatite coating has been used to enhance the stability of the coating and to increase the adhesive strength with the bone. Hydroxyapatite (HA) provides a stable zirconia implant surface into its bioactive form, enhancing its osseointegration with the surrounding bony tissue.<sup>6</sup>

There are various ways by which hydroxyapatite coating could be applied on implants. The various methods include electrochemical deposition, Sol gel dip coating, plasma spray, biomimetic deposition etc. Apart from this, the accuracy at which the coating is applied is the key.<sup>2,3,7</sup>

**Factors favouring hydroxyapatite coating:****a. Thickness**

It should not be too thin or thick. The ideal thickness of HA coating must be used to provide the expected results.

**b. Texture of the surface**

Texture and roughness define the quality of the bone and growth of blood capillaries around the zirconia dental implant. It is measured as the roughness (Ra) and porosity over the zirconia dental implant surface.

**c. Homogeneity**

Next factor is of course the uniform thickness of the HA coating. Throughout the zirconia dental implant, the uniform thickness must be maintained as the unevenness could impact on its performance.

**d. Antibacterial/germicidal properties**

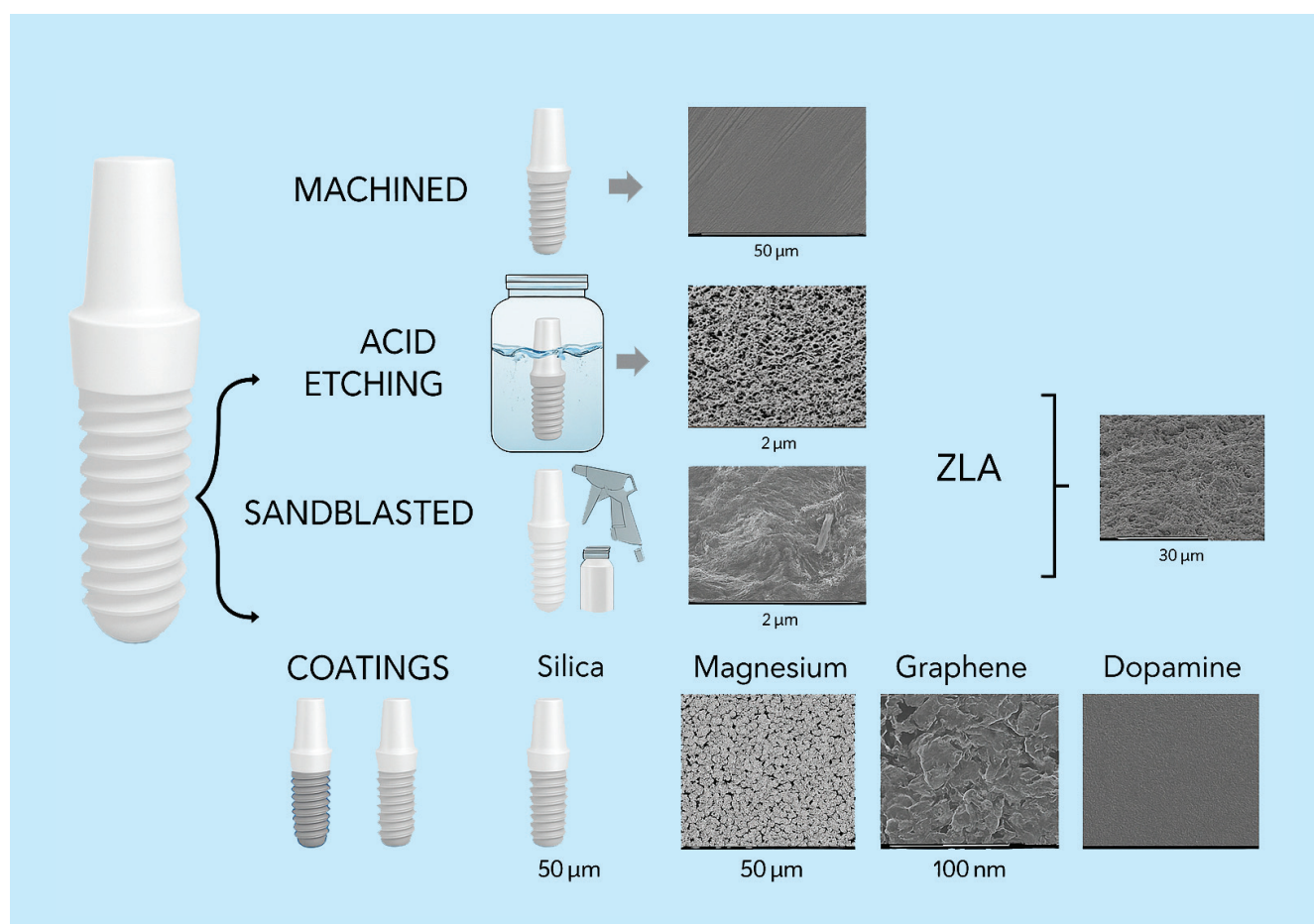
HA with anti-bacterial properties produced to fight against an infection, which is considered to be one of the common reasons for zirconia dental implant failure. Thus, the antibacterial hydroxyapatite coating on zirconia dental implants can lower the failure rate.

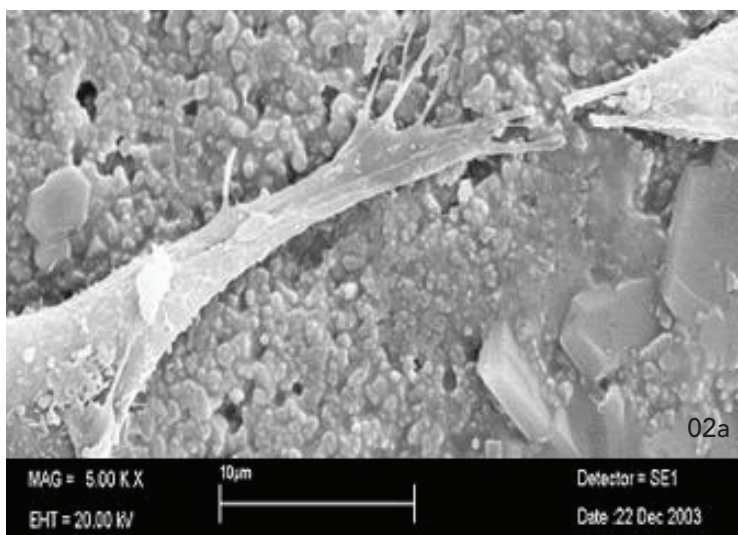
**Literature review**

Calcium phosphate (CP) is considered bio-active and stimulates bone regeneration due to their chemical composition somewhat like that of the mineral phase of human bone commonly referred to as biological apatite. But the purest form of CP coatings have shown poor attachment and stability with a weak bonding strength to the implant. To overcome these difficulties of pure CP coatings, studies have used tri-calcium phosphate reinforced hydroxyapatite coatings on zirconia surfaces, with open pores which are larger than  $100\mu\text{m}$ , a bonding strength of 24 MPa showing a high interfacial bonding between coating and substrate. In addition to this, the coatings exhibited bioresorbable and osteoconductive bone properties.<sup>8,9</sup>

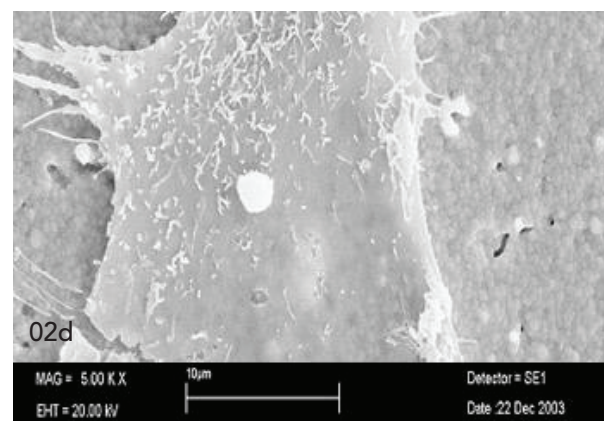
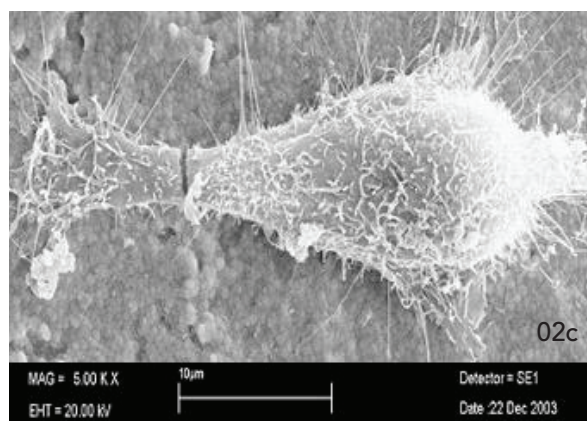
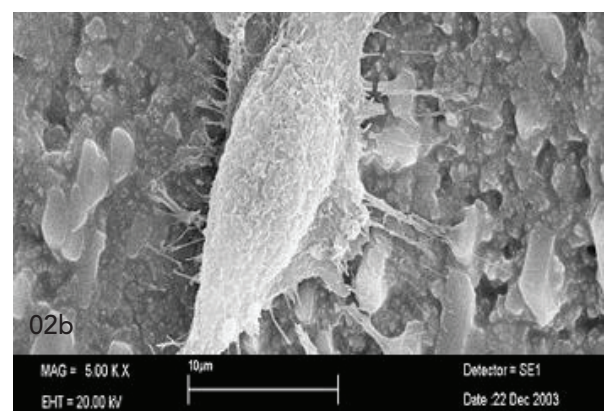
CP based coatings are produced by plasma spraying techniques in industries due to its versatility. Despite its several problems such as variation in coating bond strength with implant and modification of hydroxyapatite structure, this technique provides a good deposition rate and lower cost. New techniques for surfacing CP based coatings are

**01**  
Schematics and SEM images on different zirconia surface modifications: machined, acid etched, grit blasted, ZLA, and multi-layered coatings.





**02a–d**  
SEM image of Osteoblast morphology on Bioverit-coated zircon dioxide with a heavily roughened surface (a), Osteoblast morphology on Bioverit-coated zircon dioxide with a heavily roughened surface (b), Osteoblast morphology on zircon dioxide (c), Osteoblast morphology on zircon dioxide (d).



constantly being produced to address the problems associated with plasma spraying. In an *in vitro* study by Pardun et al., proposed a HA coating by wet powder spraying using a double action airbrush spray over zirconia. The added advantage of WPS is its versatility in coating curved surfaces with varying thickness. These experiments revealed that the hydroxyapatite dissolution stimulated the adhesion and proliferation of osteoblast cells.<sup>10</sup>

Electrophoretic deposition has been developed as a better option to the traditional techniques due to its high versatility and simplicity. A novel approach that combines both plasma electrolytic oxidation and electrophoretic deposition has been used to produce and coat HA film on zirconia.<sup>11</sup>

Hydroxyapatite has been used to coat zirconia to achieve a stable zirconia implant surface into a bioactive form, enhancing its osseointegration with the surrounding bone. In a study by Kim et al., the structure and crystal phase of the sol-gel-based HA coating layer were controlled by adjusting the sintering temperature. The optimised HA coating demonstrated superior coating stability as well as osseointegration without showing byproduct phases, which is one of the major problems of HA-coated zirconia systems. The results of this study suggested that a low-temperature sintered sol-gel-derived HA coating would increase the potential of zirconia in dental implant application.<sup>12</sup>

Aboushelib and Shawky in a study evaluated the osteogenic activity of hydroxyapatite filled porous zirconia



scaffolds resulted in a significantly higher amount of new bone formation than the scaffolds without hydroxyapatite. In addition to this, it has been known that the bioactivity can be increased to a fair extent by filling the prepared porous zirconia with hydroxyapatite. Porous zirconia filled with hydroxyapatite by physical diffusion can release hydroxyapatite particles within the bodily environment.<sup>13</sup>

In another study by Hun Kim, zirconia discs along with screws were produced by hot press injection moulding technique (IMT) using granular zirconium dioxide of dia 200–500nm. To elevate the bioactivity of the produced zirconia, nano-hydroxyapatite of dia 20–70nm was chemical bonded with the surface and then type 1 collagen was chemically bonded on it. Hydroxyapatite along with type 1 collagen was successfully coated to the zirconia through covalent bonding (chemical). It was confirmed that both nano-hydroxyapatite immobilised zirconia and type I collagen immobilised zirconia exhibit superior bioactivity through *in vitro* osteoblastic cell experiments.<sup>14</sup>

An ideal hydroxyapatite coating should be thin (<50µm) and uniform, have high adhesive/attachment strength to withstand heavy shear forces, greater hardness to reduce wear, and along with sufficient roughness and porosity to promote inward growth of the bone.<sup>15</sup>

A hybrid laser engraving combined with laser sintering of HAp resulting in the mechanical interlocking of apatite in the grooves created was suggested for zirconia dental implant applications. But the defects created at the surface below the HAp coating could be detrimental to strength. Recently D. Faria et al., suggested green state laser surface texturing and laser sintering as a promising alternative for a mechanical interlocking assisted improvement in bond strength between the zirconia substrate and HAp coating. Cho et al. reported a novel aerosol coating technique to deposit a thin, dense, and uniform coating of highly crystalline HAp on zirconia surfaces with good wettability and osteogenic response.<sup>16,17</sup>

In a recent study by Seesala et al., proposed a novel ceramic dough processing technique to form a gradient composite coating of HA in a zirconia matrix, on net shaped zirconia dental implants without compromising the features like threads. Initially, the dental implants were near net shaped on alumina-toughened zirconia (ATZ) green blanks produced through extruding ceramic dough. After sintering and cooling to room temperature the implants were coated with a slurry containing 10 Vol% HAp in the ATZ, which is also produced through the same ceramic dough processing to facilitate a quick uniform dispersion of HAp secondary phases in zirconia matrix. The final sample after drying was heat treated at a comparatively lower sintering temperature facilitating a HA zirconia composite coating on net shaped zirconia substrate. This approach is compatible and a promising solution for currently available bioinert zirconia implants.<sup>18</sup>

Some innovative methods of coating include a study by Yuan and Golden, where they used HA coating with the help of electro deposition. The substrates were coated with double layers to reduce the contact of the implant with body fluid. After this, heat treatment was carried out to samples in a vacuum (800 °C) or in the presence of air (600 °C). The benefit of double layer coating was to increase the uniformity with high adhesion between surface and HA. One more innovative method where the oxide layer was introduced in



Variety of Choices



between the implant and HA. The oxide layer protects the surface and prevents the release of toxic ions from the top layer. The oxide layers covered with HA coatings enhance the adhesion of oxide and HA. This coating also enhances the biological performance of the implant.<sup>19</sup>

Another innovative technique was the combination of two coating methods to produce HA films performed by Jia et al. The researchers coupled micro-arc and sol-gel processes together to form coating layers. The micro-arc improved the biocompatibility of the implant, and the bioactivity was enhanced further by the sol-gel HAP coating.<sup>20</sup>

To avoid implant associated infections, the medical implants are coated for antimicrobial behaviour. Ferritin, an iron storage protein, is also being explored for use in implant coatings to potentially enhance bone growth and reduce inflammation.<sup>21</sup>

## Discussion

The main target of this review is to gather a literature bank associated with the hydroxyapatite coatings for the development of metal-free zirconia implants. HA coatings, especially nano crystals of HA, enhance the biocompatibility of zirconia implants more which mimic the implant-like natural bone.

The thickness of the coating varies up to several microns with minute carbide formation providing porous surface and acceptable strength to coating. Sol-gel method can provide a range of HA precursors in aqueous form for coating on any shape of the zirconia implant. Electrochemical deposition also uses raw material in aqueous form for coating over zirconia implant. The concentrations in a wide range can be used for coating on various designs of the implants.

Ceramic implant materials have a high elastic modulus, chemical stability in the human bone, and good optical properties for aesthetics. The high modulus of elasticity results in stress shielding effect of the hard tissue, leading to local bone resorption around the implant. Hydroxyapatite coated bioactive zirconia are reactive to the surrounding tissue and establish chemical bonds with adjacent tissues. Also, these bioactive materials exhibit comparable modulus of elasticity to hard tissues (bone, enamel, or dentine), which reduces the stress shielding effect. The osteoconductive CP glass coating speeds up the osseointegration process and prevents micromotion of the interface between zirconia and bone. In addition, the outer surface of this layer acts as an encapsulation, preventing hydrothermal degradation of the YTZP.

Another important area that needs to be explored is the use of HAP in combination with other calcium magnesium phosphates naturally present in bones. These other phases have important functions during bone tissue healing. Whitlockite is one of the calcium magnesium phosphates that is naturally present in bone and plays an important role because of its osteogenesis properties. Synthesis of

whitlockite is a very critical process and requires extensive optimisation of parameters like pH and temperature. It can therefore be the reason for not exploring the coating involving different other phases, particularly whitlockite that has not been investigated comprehensively. Following this, HAP in combination with different ions substituted whitlockite can also provide better osteogenic properties.

Coating implants with hydroxyapatite and bioferritin can enhance osseointegration and bone healing by mimicking natural bone structure and potentially delivering iron for bone formation, improving bioactivity and biocompatibility of the zirconia implants.

Few drawbacks of HA-coated bioactive ceramics is that they are relatively weaker and unstable, which reduces the performance of zirconia implants. Also, the stability of coating was reduced by a byproduct, which is produced during the high temperature sintering process.

## Conclusion and future perspectives

The scope of surface modification techniques on zirconia, especially hydroxyapatite, to improve cellular response in implant dentistry, is still ongoing, but very promising. Hydroxyapatite coating is one of the simplest ways to enhance the osteoconductivity of zirconia dental implants. Thus, the use of HA coating and the use of biphasic coatings, particularly combining HAP with other available calcium magnesium phosphates, are prospective options in this area for the future. Hydroxyapatite and bioferritin coating are yet another field which needs to be explored for effectiveness and safety.

Hydroxyapatite has certain drawbacks, including fracture toughness, brittleness and low tensile strength, which if overcome could be the most promising surface technique for ceramics/zirconia dental implants.

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Literature



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