

CALCIUM PHOSPHATE NANOCOATINGS IN DENTISTRY

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Abstract:

The concept of nanocoatings was given by Chai et al., 1995 so as to enhance the mechanical as well as biological properties of Hap (hydroxapatite). This material does not have ideal mechanical properties and due to its bulk porosity, HAP can't be used to take up load, and is therefore used for coating for utilizing its ductility of the substrate level. One can increase the mechanical properties of HAP by forming HAP nanocoatings. It can be achieved when HAP is united with other nanoscale based materials as secondary phase. Thin films of polymer(biodegradable) with gentamicin have been mixed to function as 'composite coatings' for metallic implants as well as devices which fix fractures to keep away from infections associated with implants. Calcium phosphate can imitate structure as well as composition of bone mineral called normal hydroxyapatite (HAP). Thus, it becomes

a perfect alternative when thinking of an appropriate biomaterial in order to replace and imitate bone such as in case of an implant. Calcium phosphate has a special consideration on its introduction in the dental fields as it is chemically similar to bone of a human being, especially in terms of its characteristics of dissolution which enables the growth as well as regeneration in bones. Calcium phosphate nanocomposite coatings are merged with other materials which are micro or nanosized which increases its mechanical properties. Development of a newer generation of nanocomposite coating is recently being known which have nanomaterials like bioglass, carbon nanotubes as well as collagen to enhance 'osseointegration'. The initiative of nanocoatings and nanocomposites is to develop the biological and mechanical properties of calcium phosphate and alter properties related to surface of implants which are used in dentistry to speed up the process of healing and thus nanocoatings are being introduced in dentistry.

Keywords: *calcium phosphate, nanocoating, nanocomposite, implants*

Background:

In nanocoatings, either the thickness of coating is in nanoscale or the particles of the second phase distributed within the matrix are in the range of nanometers or the coatings have phases or grains of nanosizes, etc. Nanocoatings are named so because of their film size which is thinner than the microsized coatings, i.e. below 100nm for a single coating. There have been many proven benefits of nanocoatings like its ease of application methods and synthesis, purity because of the selection of the raw materials, as well as its capacity to get incorporated with different nanoparticles which in turn fabricate nanocomposite coatings. Nanocomposite coatings are demonstrated as mixture of multiple materials which consists of one 'matrix material' along with other particles in the range of nanometer scale. The matrix in this case should be a polymer which is biocompatible, a ceramic or a metallic material.(1) Nanostructured coatings have freshly fascinated growing interest due to the potential of synthesizing materials with exclusive properties, like high hardness, wear resistance, toughness, optical transparency, which makes them technically attractive for various applications from biomedical to industrial. Nanocoatings have a number of advantages for applications in the medical, aerospace, defense, oil and marine industries, which have motivated the manufacturers to include such coatings in the products which can have multiple functions. Nanocoatings have exceptional mechanical properties and increased bioactivity due to their nanocrystalline structure resulting in their large surface areas. Nanomaterials along with their developed forms, like nanocoatings and nanocomposites, present many eye-catching potentials in the field of tissue as well as implant engineering for its applications in oral and maxillofacial areas (Ben-Nissan and Choi, 2006).(2)

The concept of nanocoatings was given by Chai et al., 1995 so as to enhance the mechanical as well as biological properties of HAp (hydroxapatite). It has been clarified earlier that this material does not have ideal mechanical properties and due to its bulk porosity, HAp can't be used to take up load, and is therefore used for coating for utilizing its ductility of the substrate level. One can increase the mechanical properties of HAp by forming HAp nanocoatings. It can be achieved when HAp is united with other nanoscale based materials as secondary phase. (2)

Many nanocoating methods have been planned and a few have been applied commercially. Amongst these, the sol-gel approach has been a cost effective and bendy method which can be used for synthesis of calcium phosphate from the solutions chemically. This nanocoating's

technique based on sol-gel formula with a suitable chemistry from metallic to ceramic implants is utilized in a variety of ceramic oxide materials which are biologically compatible (Al_2O_3 , TiO_2 , partially stabilized zirconia, SiO_2 and Ta_2O_5) as it increases wear resistance, strength and curtails metal ion release to the adjacent tissues. (3)

Thin films of polymer(biodegradable) with gentamicin have been mixed to function as 'composite coatings' for metallic implants as well as devices which fix fractures to keep away from infections associated with implants. (4) As they have the affinity to fill-up and free-up pharmaceuticals and minerals and also the potential to mortify with time and the use of these films are advantageous. Also by manipulating the size of the pores and interconnectivity of such particles, the drug release rates it can be customized for the treatment. The initiative of nanocoatings and nanocomposites is to develop the biological and mechanical properties of calcium phosphate and alter properties related to surface of implants which are used in dentistry to speed up the process of healing and thus nanocoatings are being introduced in dentistry. (2)

CALCIUM PHOSPHATE AS NANOCOATINGS:

Introduction to calcium phosphate and Hydroxyapatite

Calcium phosphate can imitate structure as well as composition of bone mineral called normal hydroxyapatite (HAp). Thus, it becomes a perfect alternative when thinking of an appropriate biomaterial in order to replace and imitate bone such as in case of an implant. However, as calcium phosphate is naturally brittle and inorganic in nature, it needs to be further modified if we wish to use it in load bearing applications. Hydroxyapatite is an osteoconductive, bioactive and biocompatible material. (5) It is formulated as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. LeGeros and Ben-Nissan stated that "bone-like apatite can be better described as carbonate HAp and approximated by the formula: $(\text{Ca},\text{Mg},\text{Na})_{10}(\text{PO}_4,\text{CO}_3)_6(\text{OH})_2$ ". (6) The impurities like sodium, magnesium and carbonate can aid in enabling the bone to function in proper manner. The calcium to phosphorous ratio of bone apatite can vary within 1.37 and 1.87. This is away from the 'stoichiometric ratio' of hydroxyapatite(1.67). Hence, hydroxyapatite can be designated as a form of bone apatite which is chemically ideal and is biocompatible within the living environment. (1)

Calcium phosphate has a special consideration on its introduction in the dental fields as it is chemically similar to bone of a human being, especially in terms of its characteristics of dissolution which enables the growth as well as regeneration in bones. Hap, calcium phosphate as well as β -tricalcium phosphate have been studied immensely and applied in clinical practice because of its excellence as materials which can repair and replace bones. The nanocomposite coatings approach manipulates the mechanical properties like the strength as well as the Young's modulus of the composites together to that of the bone in its natural form, with assimilation of minor nanoparticles. (2)

When the calcium phosphate nanocomposite coatings are formed, it is merged with other materials which are micro or nanosized (like carbon nanotubes as the secondary phase) which increases its mechanical properties as the calcium precursors are produced from calcium phosphate nanocoatings which have thickness between 20 and 1000 nm on multiple substrates which use calcium nitrate and calcium acetate. Development of a newer generation of nanocomposite coating is recently being known which have nanomaterials like bioglass, carbon nanotubes as well as collagen to enhance 'osseointegration'. (1) Calcium phosphates

can be differentiated by various solubilities—for example, while they bond to the tissues present adjacently—or the capacity to degrade or replacement by advancing bone growth.

Upon contact between body fluids and calcium phosphate/HAp, there is an exchange of surface ions with the ions of aqueous solution; on the other hand, a mixture of ions and molecules(collagen and protein) are also adsorbed on the surface (Choi and Ben-Nissan, 2007). (2)

Primarily, calcium phosphate is used as a coating(bioactive) to create a tough and fast attachment(biological) to the bone. The process of firm bonding between implant or prosthetic component and the bone of the host through bone in growth is known as 'biological fixation'. This does not involve mechanical fixation or adhesives. (2)

Mudenda et al. learned recently that the evolution of microstructure of the nanocoatings of calcium phosphate is roughly of thickness 400 nm on titanium substrates(wet and dry-etched micro-patterned). Another observation was that the calcium phosphate grains were bigger on the nanocoatings over wet-etched substrates as compared to those on dry-etched substrates. Upon these set of observations, it was recommended that substrates which are functionalized and configured geometrically may be crucial in the improvement of the interface of bone and implant. It was also assured that the substrates, if patterned can possess best crystallinity of calcium phosphate as well as roughness to increase 'osteointegration' and attach cells of the bone to the surface of implant which is patterned. (7)

IMPLANTS

Biomaterials used should stimulate the surrounding tissues to enhance the in growth of implants.

In case of an implant (dental or biomedical), the prevention of osteolysis and also inflammatory response is a prerequisite, irrespective of the material of the implant.

Coating these implants with nanocoatings and nanocomposite improves the bioactivity and prevents corrosion. It releases particles as well as metal ions. This further leads to an improved structure as well as environment for the new bone's growth. The raised issues and concerns about adhesion and other biological interactions regarding the increase of longevity and dependability have forced the experiments of alteration of the surface with respect to a raise in the bioactivity, rapid healing and bone-implant adaptability from last two decades.

Calcium phosphates have been used as a material for coating metallic implants for its utility in dentistry and orthopedics since early 1980s. (1)

Jimbo et al in 2011 additionally presented proof in favour of the fact that surface coated with calcium phosphate improves the procedure of osteointegration. He later observed that the bone around the implant is progressively mineralized. In addition to this, adenosine triphosphatase, which is a marker of osteoclast significantly higher for implants which are coated, showed a steady resorption of the calcium phosphate coating. (8)

Furthermore, titanium has the potential to enhance the application of calcium phosphate coatings which are structurally nanosized in both natural as well as artificial grafts which increases its usage as a well-suited biomaterial for soft tissue.

When Kadono et al examined the efficiency of nanocoated-polyester vascular grafts used for implants in canine carotid arteries, they explained that CaP nanocoatings could help in

reduction of giant cells and inflammatory cells during construction of tissue around vascular grafts having composition of synthetic polymeric materials. (9)

The efficiency of these nanocoatings for regenerating the tissues was tested by Yang et al. Upon examining the cell seeded scaffold under the electron microscope, he led the hypothesis that the nanocoating of silk scaffold were appropriate for tissue growth.

Tissue response to an implant material

When a biomaterial is inserted within a tissue in form of an implant, various tissue responses are likely to occur at the interface between the material and the hard or the soft tissues in the region. Previous studies and reviews have identified five different possibilities of interfacial responses of tissue to an implant. (1) These are as follows -

- In case the material is biodegradable and non toxic, it will be replaced by the tissue which is surrounding the material.
- In case the material is non toxic and biologically inactive, the implant can be ultimately isolated due to formation of a fibrous tissue
- In case the material is biologically active and non toxic, osteointegration will occur, i.e. there will be formation of an interfacial bond
- In case the material is bioinert and non toxic, ankyloses will occur if the bond is weak and bone cements will form if it is strongly bonded with external cements.
- In case the material of implant is toxic, the surrounding tissues of the body will die

Implant materials

For a very long time, numerous materials have been considered as implant materials based on their properties. The two most important criteria for their consideration as a long term success have been biocompatibility and cytotoxicity of the material. Amongst these materials, calcium phosphate has been one of the most accepted to its chemically similar nature to human bone. The best part of using calcium phosphate is its dissolution characteristics when it binds with the tissue as well as its ability of degradation and replacement by promoting bone growth.

Following is the Solubility of different calcium phosphates: Amorphous calcium phosphate > dibasic calcium phosphate > tetracalcium phosphate > α -tricalcium phosphate > β -tricalcium phosphate > Hap (10)

CALCIUM PHOSPHATE NANOCOATING IN DENTAL IMPLANTS

The roughness of the surface of an implant influences the quality as well as the rate of osseointegration. (Wennerberg et al. 1995b). There are various ways of coating implants with calcium phosphate in which roughness of the implant surface can be increased like etching, plasma spraying, deposition method assisted by ion-beam, etc. (11)

A study where CaP was used as a nanocoating material on implant. The study involved smooth basal surface and rough basal surface. Calcium Phosphate was nanocoated (thickness of 500nm) by the IBA method. The results of these nanocoating were very successful in dogs (Choi et al. 2011; Song et al. 2009; Chae et al. 2008). After 12 weeks of healing, both smooth and rough surface of CaP nanocoating had very good histological as well as statistical results with regard to bone-implant contact in control group. (11)

Two mechanisms of endosseous integration was explained by Davies (1998): 1) Distance osteogenesis is a mechanism where the new bone will reach the surface of implant from

existing peri implant bone by appositional growth. 2) In Contact osteogenesis or osteoconduction mechanism, the new bone will be formed on the implant surface directly. Distance osteogenesis was comparatively faster in rough surface CaP than in smooth surface CaP. Both distance and contact osteogenesis have good resolution in rough surface CAP coating. This confirms that the rough surface of implant is effective in cellular response in formation of the new bone around the defect. Rough surface of Implant has better efficacy to induce growth of bone even in the far lateral part of defect. Boyan et al. (1996) explained the influence of surface roughness on the cellular response to an implant. Mesenchymal cells on rough surface will lead to formation of focal attachment and reach the spaces in between surface peaks. This could result in expression of a particular phenotype that will favour the osteogenesis. Surface roughness due to CaP coating could also facilitate vascular ingrowth favourable for osteogenesis. Calcium Phosphate is very efficient as nanocoating on implant given that the changes in surface energy lead to physical effects and enlarge the surface area. Also the chemical interaction between Ca^{2+} and CaPs binding proteins contributes to its efficiency. (Sul et al. 2002 ; Feng et al. 2002). Calcium phosphate also plays viral role in increasing bone-implant contact. (11)

CONCLUSION

The implant materials like titanium or its alloys (Ti-6Al-4V) are used successfully for other prosthesis and dental implants since 25 years. But it is observed that adherence of cells to most metal surface is not adequate. Intimate tissue in-growth is considered as the most appropriate mechanism for better the adherence. In order to fasten the healing process, surface properties of implants are enhanced by the nanocoatings. Over the previous decade, the interest in nanostructured materials has increased tremendously in the fields of medicine as well as dentistry. There has also been rise in application of nanocoatings and nanocomposites in bone grafts, implants and involved slow drug delivery system in biomedical and dental materials.

The effect of nanotechnology is considered to be very beneficial. However, we still need to consider the possible risks associated with it. Presently, the authoritarian standards prevailing use of nanomaterials for applications in dentistry are not enough and there are no efficient methods which can assess the long-term risk of exposure in patients. All calcium phosphates are however non-toxic as well as biodegradable, hence not posing a problem in the long run. However, inconvenience may arise due to incomplete safety and toxicity profiles of nanomaterials, which may successively cause a huge range of long-term medical problems. The amendment of surfaces has become a very important element to recognize the influence of chemical and structural properties on interactions between the material and the tissue. It can be expected that modifications in the surface in order to control tissue response shall open up various paths for growth of superior dental and maxillofacial implants and devices and at a faster rate than the present one and in a more systematic manner.

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