Corrosion Resistance of Fluorapatite Nanoparticles: A Brief Review with a Focus on Biomedical Applications

Otpornost nanočestica fluorapatita na koroziju: Kratki pregled sa fokusom na biomedicinske primene

Dušan Milojkov[1,*], Miroslav Sokić[1], Vukosava Živković-Radovanović[2], Gvozden Jovanović[1], Vaso Manojlović[3]

[1] *Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade, Serbia*

[2] *Faculty of Chemistry, University of Belgrade, Serbia*

[3] *Faculty of Technology and Metallurgy, University of Belgrade, Serbia*

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*d.milojkov@itnms.ac.rs

Abstract

Fluorapatite (FAP), a calcium phosphate compound, has gained significant attention as a promising material for various biomedical applications due to its excellent biocompatibility, osteoconductivity, and resistance to corrosion. The incorporation of fluoride ions into the crystal lattice of FAP enhances its structural stability, making it less susceptible to degradation in biological environments. FAP nanoparticles exhibit increased surface activity, improved adhesion, and a pronounced barrier effect compared to microparticles, which makes them highly suitable for use in protecting metal implants from corrosion. This review provides an overview of corrosion resistance of FAP nanoparticles, focusing on the mechanisms that contribute to this property and its implications for biomedical applications. Key aspects such as FAP synthesis methods, bioactivity, and its role in bone regeneration, dental materials, and implant coatings are explored. Additionally, the mechanisms of corrosion protection offered by FAP, including surface passivation and the role of fluoride ions, are discussed in detail. Finally, the biomedical significance of these properties is evaluated, with an emphasis on their potential to improve the longevity and performance of implantable biomaterials.

Keywords: *fluorapatite; corrosion; biomedical applications; implants; bioactivity*

Izvod

Fluorapatit (FAP), jedinjenje kalcijum-fosfata, privuklo je značajnu pažnju kao obećavajući materijal za različite biomedicinske primene zbog svoje izuzetne biokompatibilnosti, osteokonduktivnosti i otpornosti na koroziju. Uključivanje fluoridnih jona u kristalnu rešetku FAP-a poboljšava njegovu strukturalnu stabilnost, čineći ga manje podložnim degradaciji u biološkim sredinama. FAP nanočestice pokazuju povećanu površinsku aktivnost, bolju adheziju i izraženiji barijerini efekat u odnosu na mikročestice, što ih čini veoma pogodnim za primenu u zaštiti implantata od korozije. Ovaj pregled razmatra otpornost na koroziju FAP nanočestica, sa fokusom na mehanizme koji doprinose ovoj osobini i njenim implikacijama za biomedicinske primene. Ključni aspekti, kao što su metode sinteze FAP-a, bioaktivnost i njegovu ulogu u regeneraciji kostiju, dentalnim materijalima i premazima za implantate, istraženi su u ovom radu. Takođe, detaljno su razmatrani mehanizmi zaštite od korozije koje FAP nudi, uključujući pasivaciju površine i ulogu fluoridnih jona. Na kraju, biomedicinski značaj ovih osobina je evaluiran, sa naglaskom na njihov potencijal da poboljšaju dugovečnost i performanse implantabilnih biomaterijala.

Ključne reči: *fluorapatit; korozija; biomedicinske primene; implantati; bioaktivnost*

Introduction

The field of biomaterials has undergone significant advancements in recent decades, driven by the increasing demand for medical implants and tissue regeneration solutions. Bone and dental implants, which must integrate well with the surrounding tissue and function reliably over time, are key areas where materials science plays a crucial role. To meet these demands, researchers have focused on developing materials that are biocompatible, bioactive, and possess long-term stability in physiological environments. Among the various materials being explored, calcium phosphate ceramics, especially fluorapatite (FAP), have emerged as promising candidates for biomedical applications.

Fluorapatite ($Ca_{10}(PO_4)_6F_2$) is a calcium phosphate compound that is structurally similar to natural bone and tooth mineral [1, 2]. What sets FAP apart from other calcium phosphate materials, such as hydroxyapatite (HA), is the substitution of hydroxyl groups with fluoride ions in the crystal lattice [3]. This substitution has a significant impact on the stability of the material, particularly in environments where the pH decreases, such as the oral cavity during acidic reactions caused by bacterial activity [4, 5]. Fluorapatite's unique properties make it an attractive material for use in dental and orthopedic implants, as well as for applications in bone tissue regeneration.

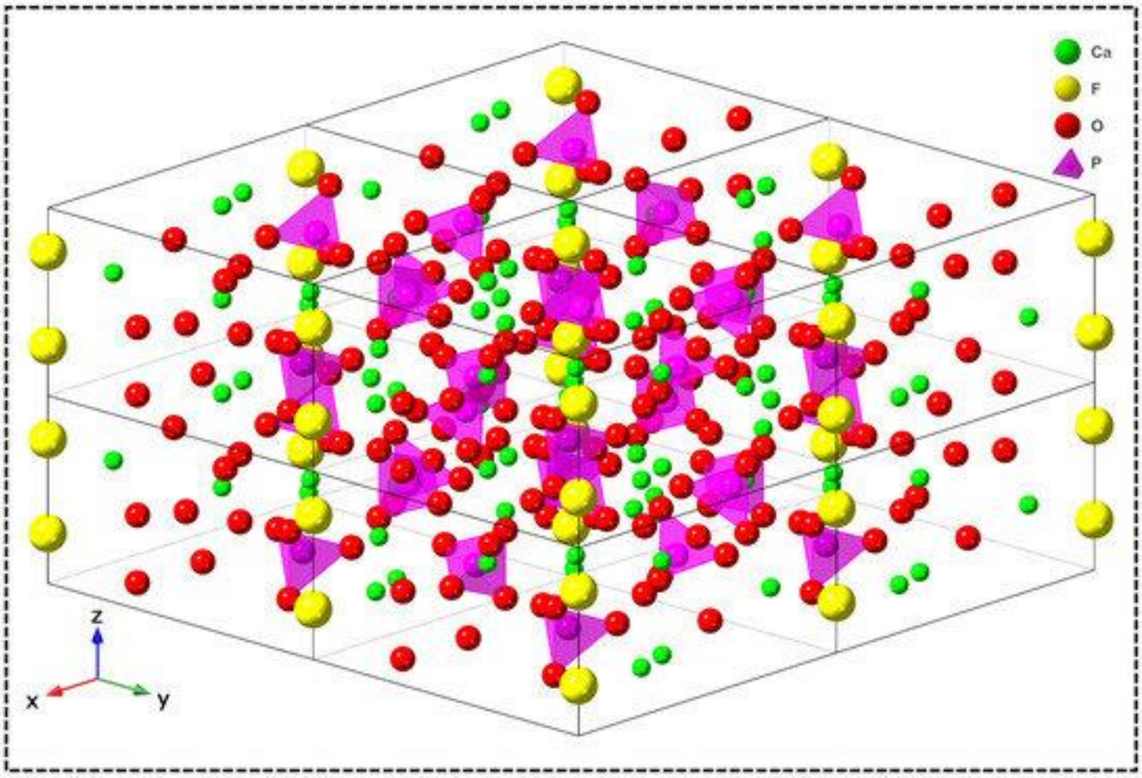

Figure 1. *Crystal structure of FAP. Reprinted from [3] under CC BY 4.0.*

One of the key challenges in the long-term success of medical implants is their corrosion resistance. Implantable materials must maintain their integrity when exposed to biological fluids, which can be corrosive. The degradation of implant materials not only compromises their mechanical strength but can also result in the release of ions that might cause inflammatory responses or even lead to implant failure [6, 7]. Titanium and its alloys, as well as stainless steels, are commonly used in medical implants but are susceptible to various forms of degradation in the presence of body fluids containing chloride ions [6, 7]. The corrosion of metallic materials represents one of the key challenges in materials engineering, particularly in biomedical applications, where implant damage can lead to serious health complications. Therefore, corrosion resistance is one of the critical criteria for evaluating biomaterials for use in clinical settings.

This review aims to explore the corrosion resistance of fluorapatite nanoparticles, focusing on the mechanisms that contribute to this stability and the material's biomedical relevance. By examining the chemical structure, synthesis methods, and biomedical applications of FAP, this paper will provide a comprehensive understanding of why FAP is a suitable candidate for long-term use in the human body. The review will also address how the fluoride ion substitution contributes to enhanced corrosion resistance and the material's overall biocompatibility.
Furthermore, we will discuss the significant biomedical applications of FAP in bone regeneration, dental materials, and implant coatings, with particular emphasis on its role in maintaining stability under physiological conditions. As research in this field continues to advance, understanding the interplay between structure, corrosion resistance, and bioactivity in FAP will be critical for developing improved biomaterials for medical use.

Characteristics of Fluorapatite Influencing Corrosion Resistance

Fluorapatite (FAP) exhibits a unique set of properties that contribute significantly to its corrosion resistance and overall stability as a biomaterial. The key feature that differentiates FAP from other calcium phosphate materials is the presence of fluoride ions within the crystal structure, which replaces the hydroxyl groups typically found in hydroxyapatite (HA). This substitution has profound implications on the chemical stability and dissolution behavior of the material.
Fluoride substitution in the FAP crystal lattice strengthens the ionic bonding between calcium and phosphate ions. This structural modification reduces the material's solubility, particularly in acidic conditions [8, 9]. In biological fluids, which can range in pH from slightly acidic to neutral, the fluoride ions help maintain the integrity of the material by preventing the rapid dissolution that is observed in materials like HA under similar conditions [10, 11]. This enhanced stability makes FAP less susceptible to pH fluctuations, which is particularly advantageous for its use in the human body, where acidic environments can lead to degradation of other biomaterials.
The fluoride ion substitution also has a thermodynamic effect, reducing the free energy of dissolution and, consequently, the tendency of FAP to undergo solubilization when exposed to simulated body fluids (SBF). This makes FAP an ideal candidate for long-term use in environments where other materials would experience significant degradation.
In addition to fluoride substitution, the surface chemistry of FAP plays a crucial role in its corrosion resistance. When used as a coating on metal implant materials, FAP forms a protective layer that acts as a passivating barrier between the metal and surrounding biological fluids. This layer reduces ion exchange and prevents corrosion of the underlying metal, while its biocompatible nature ensures long-term stability and reliability of the implant.
FAP's high chemical stability also allows it to maintain its bioactive properties, such as the ability to stimulate bone growth and promote the formation of mineralized tissue. These properties make it suitable for bone implants and dental applications, where stability and bioactivity are essential for successful integration with the body.

Synthesis of FAP for Biomedical Applications

Fluorapatite can be synthesized using a variety of methods, each of which impacts its structural properties, particle size, and surface characteristics. The method of synthesis plays a pivotal role in determining the material's suitability for different biomedical applications. Some of the most commonly used synthesis techniques for FAP are precipitation, sol-gel, and hidrothermal metohod [8, 11].
One of the most widely used techniques for synthesizing FAP is precipitation [11]. In this method, calcium and phosphate salts are mixed in an aqueous solution containing fluoride ions. This approach allows for the formation of FAP nanoparticles, which can be further processed to enhance their size,

shape, and surface properties. Precipitation is a cost-effective and scalable method, making it suitable for large-scale production of FAP for biomedical applications.

The sol-gel process is another common method used to synthesize FAP [8]. This technique involves the transition of a sol (a colloidal solution) into a gel-like substance, which is then heated to form a stable FAP network. The sol-gel process allows for precise control over the nanostructure of FAP, including particle size and surface area, making it particularly useful for applications where fine control over these characteristics is crucial.

The hydrothermal method involves synthesizing FAP under high-pressure and high-temperature conditions [8]. This method is particularly advantageous for producing high-purity FAP with superior crystallinity and mechanical properties. FAP synthesized through hydrothermal methods tends to have a more stable structure, which is essential for use in demanding biomedical applications such as implant coatings and bone scaffolds.

Fluorapatite has a broad range of biomedical applications due to its bioactive nature and corrosion resistance. Some of the most prominent applications include:

- *Bone Regeneration*: FAP is frequently used in the development of bone scaffolds and grafts. Due to its chemical similarity to natural bone, FAP promotes osseointegration and supports the growth of new bone tissue. It is used in orthopedic implants to enhance healing in fractures and bone defects.
- *Dental Materials*: In dental medicine, FAP is used in dental implants, fillings, and coatings. FAP's ability to bond with natural tooth enamel and resist corrosion in the mouth makes it ideal for long-lasting dental restorations.

Implant Coatings: FAP is often applied as a coating on metallic implants, such as titanium and stainless steel, to improve their biocompatibility and corrosion resistance. This coating helps prevent the release of metal ions into the surrounding tissue, reducing the risk of inflammatory reactions and implant failure.

Mechanisms of Corrosion Protection and Biomedical Significance

Fluorapatite's resistance to corrosion is governed by several key mechanisms that ensure its stability and biocompatibility in the body.

The surface passivation of FAP plays a crucial role in its corrosion resistance. When exposed to biological fluids, a passivating layer forms on the surface of the material, preventing further degradation. This passivation reduces the solubility of FAP in physiological environments, ensuring that the material maintains its structural integrity over time.

Fluoride ions significantly enhance the chemical stability of FAP by reducing its solubility in acidic environments. This is particularly important for long-term implants that may be exposed to acidic body fluids. Fluoride also plays a key role in promoting surface protection, making FAP highly stable even in aggressive biological conditions.

The corrosion resistance of FAP ensures that implants made from this material maintain their mechanical strength and bioactivity over time. This stability is critical for the long-term success of implants, as it prevents the release of harmful ions into the surrounding tissue. FAP's ability to withstand degradation while promoting bone regeneration makes it a reliable material for use in bone implants, dental materials, and orthopedic prostheses.

Table 1 summarizes selected studies investigating the corrosion behavior of FAP, its composites, and coatings on metallic substrates. These studies collectively demonstrate the strong potential of FAP for enhancing corrosion resistance in biomedical devices.

Recent studies have further demonstrated that substituting additional cations (e.g., Mg^{2+}) or combining FAP with metallic or carbon-based reinforcements can substantially enhance corrosion resistance, mechanical stability, and bioactivity. Such hybrid systems exhibit multi-functional performance, providing both mechanical robustness and chemical protection under physiological conditions [12–17].

Table 1. Summary of recent studies on corrosion resistance of FAP-based materials

Authors	Year	Material/System	Main Findings	Ref.
Sharifnabi A., et al.	2014	Mg-substituted fluorapatite coating on 316L SS	Mg–FAP coating reduced corrosion rate and metal ion release, enhancing corrosion resistance and biocompatibility.	[12]
Razavi M., et al.	2010	Mg–fluorapatite nanocomposite (AZ91–20FA)	FAP nanoparticles decreased corrosion rate and promoted apatite layer formation, improving protection and osteoconductivity.	[13]
Fathi M.H., et al.	2009	Fluorapatite/niobium (FA/Nb) composite coating	FAP/Nb coating showed lower corrosion current and improved biocompatibility compared with FAP alone.	[14]
Khani M., et al.	2022	Mg–Mn–Ca/FA + GNP hybrid biocomposite	Reinforcements enhanced mechanical strength and corrosion resistance, achieving over 15× higher impedance.	[15]
Zang M., et al.	2024	Fluorine-substituted HA coating on Ti–6Al–4V	Optimal 9 wt% CaF_2 substitution yielded highest crystallinity, strength, and lowest corrosion rate.	[16]
Razavi M., et al.	2010	AZ91–FA nanocomposites (10–30 wt% FA)	Increasing FAP content improved hardness and corrosion resistance, with 20 wt% FAP giving best overall performance.	[17]

Conclusion

Fluorapatite nanoparticles and their composites are emerging as highly promising materials for biomedical applications, primarily due to their outstanding corrosion resistance, biocompatibility, and bioactivity. The presence of fluoride ions within the crystal lattice enhances chemical stability and minimizes degradation in physiological environments. Recent research consistently demonstrates that FAP-based coatings and composites can significantly improve the corrosion resistance of metallic substrates while maintaining or even enhancing biological performance. Continued development of optimized synthesis methods and hybrid FAP systems is expected to further advance their use in next-generation medical implants, contributing to safer, longer-lasting, and more reliable biomaterials. Future research should focus on tailoring the surface functionalization of FAP nanoparticles to further enhance their corrosion resistance and biological response.

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