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"A Comprehensive Review on Electrophoretically Deposited Hydroxyapatite-Based Composite Coatings on 316 LVM Stainless Steel for Biomedical Applications"

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ABSTRACT

316LVM stainless steel is widely used in biomedical applications but suffers from localized corrosion, particularly pitting and crevice corrosion under physiological conditions, requiring surface modification. This review examines electrophoretic deposition (EPD) of hydroxyapatite (HA)-based coatings to enhance corrosion resistance, bioactivity, and Osseointegration. While HA offers excellent biocompatibility, its inherent brittleness can be overcome by reinforcingTiO2 and ZrO2 nanoparticles which enhance the coatings mechanical strength, adhesion and corrosion resistance. Overall, EPD-derived composite coatings show strong potential for improving implant performance, with further optimization and long-term in vivo validation required to confirm long-term biological performance, coating stability and clinical safety.

1. Introduction

Despite numerous studies on HA and composite coatings, there is no comprehensive review that specifically focuses on how EPD-derived HA/TiO_2/ZrO_2 coatings influence corrosion behavior, adhesion mechanisms, and bioactivity of 316LVM stainless steel, especially compared to other biomedical alloys. Bio-active metallic materials have been used in medical therapies for almost twenty years. Approximately 70 to 80 percent of medical gadgets are composed of biocompatible materials. In order to improve patients' quality of life, metallic bio-materials are crucial for treating injured tissues, particularly hard tissues, fixing fractures, and repairing bones. This is because of its exceptional toughness, strength, and durability. Because older adults are more likely to have hard tissue failure, the need for biometallic materials with exceptional mechanical characteristics is growing globally [1]. Early on in the development of metal implants, corrosion and diminished strength were issues. The type of metal used in biomedical applications depends on the specific usage of these implants. Table 1 provides a summary of the numerous metal types often used in various implant classes.[2].

Table 1. Classification of implants and types of metals used [2].

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Division	Example of implants	Types of metals
Cardiovascular	Stent artificial valves	316L SS; CoCrMo; Ti Ti6Al4V
Orthopaedics	Bone fixation(plate,screw.pin) Artificial joint	316L SS; Ti; Ti6Al4V CoCrMo; Ti6Al4V ; Ti6Al7Nb
Dentistry	Orthodontic wire filling	316L SS; CoCrMo; TiNi; TiMo AgSn(Cu) amalgam , Au
Craniofacial	Plate and screw	316L SS; CoCrMo; Ti; Ti6Al4V
Otorhinology	Artificial eardrum	316L SS

Implant materials including stainless steel, coabalt, and their alloys are widely utilized in orthopedic and dental applications because of their excellent strength, durability, and low rate of wear within the body [3].

Numerous common uses for metal implants are depicted in Figure 1 [4].

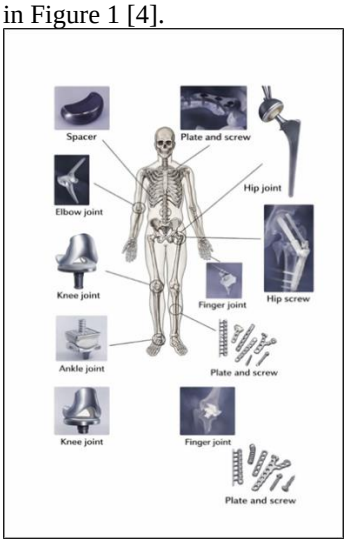


Figure1. Biomaterials for human application [4].

Stainless steel (SS) has several uses due to its high general corrosion resistance and affordability [5].

In biomedical applications, stainless steel 316LVM is frequently utilized as pulmonary and coronary stents. Stainless steel is taken into consideration for such applications since arteries require mechanical support to heal without the possibility of rebound. However, the corrosion resistance of the biomedical grade of 316LVM is much lower than that of other metallic biomaterials (such as Ti-based alloys).

When exposed to severely corrosive environments, the steel is not adequately protected by the passive layer. Since corrosion of a metallic material is one of the most crucial factors to take into account when it is created for implants, current research focuses on developing coatings for corrosion protection that do not alter the mechanical properties of the material [6].

Considering the above requirements, low-temperature surface modification processes which can be applied to all faces of geometrically complex surfaces (miniaturized implants) are worth considering. Surface modifications of metallic implants are performed by sol-gel, electrophoretic deposition, pulsed laser deposition and plasma spray technique. Electrophoretic deposition (EPD) is the technique that has been adopted for processing biomaterials, especially bioactive coatings and biomedical nanostructures [7].

Starting with highly dispersed suspensions of biomaterials in particulate form (micronized and nanoscale particles, nanotubes, and nanoplatelets), the well-known benefits of EPD for the fabrication of a wide range of microstructures and nanostructures as well as unique and complex material combinations are being used.Research is also being done on the EPD of biological entities as bacteria, cells, and enzymes. EPD is often measured in cells with only two electrodes. [8].

There are basically three steps in the EPD process [9].

• Making a stable dispersion of particles.

• The particles are moved with the help of an electric field in the direction of the depositing electrode.

•Particles being deposited on the surface of the electrode.

•The different processes involved in the EPD process are displayed in a schematic manner (Fig. 2).

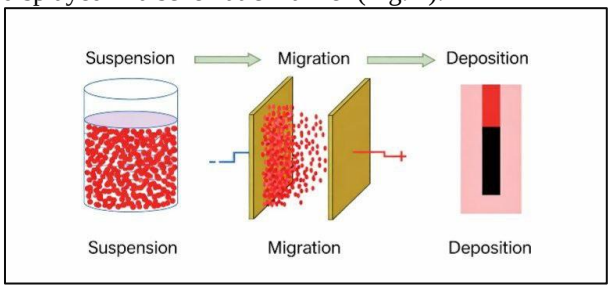


Figure 2. The EPD steps are depicted schematically [9]

Although HA is bioactive, it has poor mechanical properties and has limited applications in therapeutic

uses. The dense HA has a compressive strength 4 times higher than that of cortical bone; however, its tensile strength and fracture toughness are significantly lower.
The most important factors influencing HA's in vitro activity are its composition and crystal structure, which are the same as those of the mineral component of bone [10].
It has been demonstrated that HA enhances the osseointegration of metallic prostheses with bone tissue.In actuality, the osteoconductive properties of HA stop fibrous tissue from growing around the implant. Recent years have witnessed an increase in the use of bioactive materials for this purpose, such as bioactive silicate glass coatings, with positive outcomes [11].

To prevent corrosion and subsequent release of dangerous metallic ions into surrounding tissue, one of the best solutions is to coat metallic implants with hydroxyapatite (HA). [12].

Stainless steel 316 LVM

Because of its superior resistance to oxidation and corrosion and its exceptional formability, austenitic stainless steel is utilized extensively as an engineering material in many different sectors [13–16].
The primary obstacle to 316L stainless steel's industrial usage is the presence of coarse grains that result in low tensile strength. As a result, producing stainless steel that is both strong and ductile has emerged as a major area of study in recent years. The limits of producing components with complicated geometry make it impractical to use conventional methods of strengthening stainless steel, which call for additional tooling or treatment after fabrication [17–21].

Table 2.Chemical composition of 316LVM [22].

Element	Wt%
C	0.016
Si	0.51
Mn	1.67
P	0.023
N	0.038
S	0.001
Cr	18.14
Mo	2.59
Ni	13.27
Cu	0.18
Fe	Bal

Corrosion resistance

Ion release and pitting and crevice corrosion emphasize the necessity for surface modification or alloying to increase corrosion resistance. Due to its affordability, 316L is still widely used for temporary implants in spite of these problems. Complications resulting from the corrosion of specific implants have been brought to light by recent investigations. When Frommer et al. [23] looked at the radiological and clinical implications of corrosion with Biodur 108 alloy implants, they discovered macroscopic corrosion in more than 80% of the instances. It was proposed that variations in electrolyte concentration caused by physiological fluids seeping into the tiny space between the male portion of the implant and the crown caused crevice corrosion .
Corrosion on bolts and nail holes may also be explained by this mechanism. Similar problems with osteolysis, periosteal response, and staining (a sign of possible corrosion) after nail removal were noted in another study [24]. Although it is yet unknown if complete weight-bearing earlier in the process caused the corrosion or if the alloy itself played a role, these events mostly happened in the last phases of bone lengthening.
Crevice corrosion can result from localized passive film breakdown brought on by tiny motions or oxygen depletion in microscopic spaces.
Because orthopedic implants carry a high risk, it is crucial to assess new surface treatment methods to improve the localized corrosion resistance of austenitic stainless steels. [25–27].

Rationale and scope of the present review

Although hydroxyapatite-based coatings on stainless steel have been extensively investigated, previous reviews have generally addressed hydroxyapatite coatings across different metallic substrates, coating techniques, or composite systems without specifically integrating the effects of electrophoretic deposition (EPD), reinforcing ceramic phases, and the performance of 316LVM stainless steel within a single framework. For example, previous reviews have discussed hydroxyapatite adhesion on metallic biomaterials, the fundamentals and applications of EPD, and surface modification of other stainless-steel substrates. [1, 4, 8] However, a focused critical synthesis addressing HA-based composite coatings deposited by EPD on 316LVM, particularly with respect to corrosion resistance, coating adhesion, mechanical behavior, and bioactivity, remains limited.
The present review therefore focuses specifically on EPD-derived HA-based composite coatings on 316LVM stainless steel and evaluates the role of reinforcing phases such as TiO_2 and ZrO_2 in overcoming the inherent brittleness and limited mechanical reliability of HA coatings. Particular attention is given to the relationships among EPD parameters, coating microstructure,

adhesion, localized corrosion behavior, and biological performance. In addition, the available literature is critically compared to identify inconsistencies, methodological limitations, and unresolved research gaps that may affect the translation of these coatings toward biomedical applications.

Surface modification techniques

Biomaterial corrosion has gained increased importance especially to avoid infections and allergic reactions possible after the introduction of biomaterials in the human body. This corrosion issue has led to a number of methods being devised to change the surface to make it more resistant to corrosion.The "optimal solution" to improve corrosion resistance performance, produce greater biocompatibility, and encourage bone integration of biocompatible metals and alloys is now thought to be the introduction of surface changes. Biocompatible metals [28] include ion beam surface modification, coating deposition and passivation oxide layers.

The main selection criterion is the biomaterial's acceptance by the human body. There should be no adverse effects, such as allergies, inflammation or toxicity, immediately after the material is placed in, or subsequently, from the implant [29]. Biomaterials can be modified by a variety of widely used techniques, including covalent grafting, surface coatings and synthetic films, plasma treatment and self-assembled monolayers (SAMs). [30].

Covalent grafting Chemical and strong covalent bonding of functional molecules to the surface of a material. This technique is used to obtain a stable surface modification and has been employed for improving biocompatibility and minimizing thrombosis in biomedical applications. [31].

Surface coating techniques are widely used to enhance surface properties of materials while preserving their bulk characteristics. These techniques range from traditional methods, such as electroplating, to advanced processes like physical vapor deposition (PVD), chemical vapor deposition (CVD), and atomic layer deposition (ALD). Surface coatings play an important role in improving corrosion resistance, wear resistance, and performance in industrial and biomedical applications.[32]

Thin film synthesis involves the fabrication of thin layers of materials with controlled thickness and composition to achieve specific functional properties. Various synthesis techniques, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), sol–gel processing, and electrodeposition, are commonly used to tailor the structural, mechanical, and surface properties of thin films for applications in membranes, coatings, electronics, and biomedical fields.[33]

Plasma treatment A surface modification method that involves the alteration of the surface energy and chemical composition of a material using an ionized gas, but not changing the bulk properties of the material. The method is used extensively to increase the surface wettability, adhesion, and functionalization, and to improve the functionalization and the surface adhesion of thin films and biomedical applications..[34]

Self-assembled monolayers (SAMs) are ordered molecular layers that spontaneously form on solid surfaces through chemical adsorption. They are widely used for surface functionalization because they allow precise control over surface chemistry, wettability, and interfacial properties, making them useful in corrosion protection, biosensing, and biomedical applications.[35]

Coating for biomedical applications

Metal implants may fail during surgery due to several factors, including insufficient biocompatibility, elevated degradation rates (e.g., magnesium alloys), inflammatory responses, infections, inertness (e.g., stainless steel, titanium, cobalt-chromium alloys), low wear resistance, discrepancies in elastic modulus, excessive wear, and concealed stress. Figure 3[2] illustrates the necessity of addressing this issue by developing a method that improves the fundamental properties of metallic implant surfaces by modifications to the material's surface and shape, while preserving the mechanical attributes of the metallic implants."

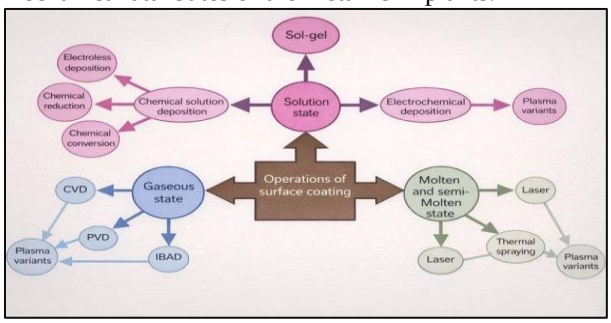


Figure 3. Abroad division of surface engineering methods[2]

There are a number of strategies that can be used, and surface modification of metals by coatings is believed to be one of the most promising methods to enhance the performance of implant materials [36]. Ceramic coatings are thought to be the best option for activating implants that come into direct touch with bones and tissues because of their dependability and effectiveness. It is due to their special qualities that make them great in terms of compatibility with the bones and stability [37, 38]. To enhance the antibacterial activity of biomaterials, coatings can be applied to the surface of materials.

The attachment of peptides to cells is enhanced by coated surfaces, which also influence alterations in host cells, extracellular matrix (ECM) proteins, and tissue growth, ultimately boosting biomaterial acceptance. Because

ceramics are crucial for improving bone regeneration and repair, coating them on biomaterials has shown encouraging outcomes in the field of orthopedic surgery [39].

Hydroxyapatite coatings

Ca5(PO4)3(OH) is the chemical formula for hydroxyapatite (HAp),a naturally occurring mineral form of calcium apatite.

"The formula Ca10(PO4)6(OH)2 is frequently used to show that the crystal unit cell is made up of two molecules. The HAp crystal structure unit cell is made up of close contact of Ca, PO4, and OH (Figure 4 [40]).

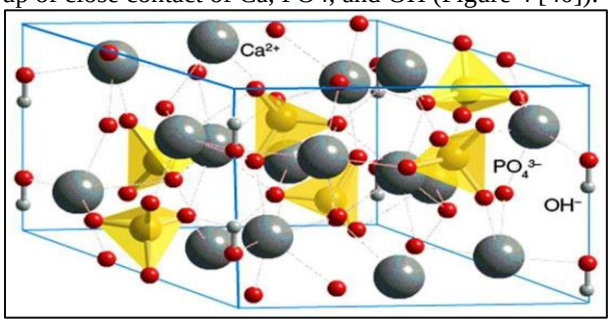


Figure 4. crystal structure of HA[40]

The main hardness constituent of dental enamel and bone minerals is hydroxyapatite. The excellent biocompatibility and activity of HA has led to its use in a wide variety of fields. Its structural similarity to the minerals in bones makes it useful in orthopedics and dental implants [41].

Titanium Oxide Coating

Titanium dioxide (TiO2) is the name of the naturally occurring oxide of titanium. It is also known as titanium. Titanium comes in many crystalline structures and is among the most frequently used ceramic materials for applications like corrosion protection coatings, water purification, photo-catalyst, self-cleaning glass, and sensor. All these industries are successfully using Titania because of its high chemical durability and thermal stability as a thin or thick coated film [42].

There are three main crystallographic forms of titania, brookite, anatase and rutile . The stability of these phases, which can also be used as nanomaterials, is dependent upon the grain size and rutile is often employed as a white pigment in polymers, with a grain size of 200–300 nm, while anatase titania is often employed as spherical particles with a diameter of ~20 nm" [43].

As seen in Figure 5, all polymorphs have a deformed TiO6 octahedral structure made up of titanium cations that are six-fold coordinated to oxygen anions. The octahedral edges of these structures are shared (some also share corners). The crystal forms of titania are revealed by the TiO6 octahedral building block arrangement [44].

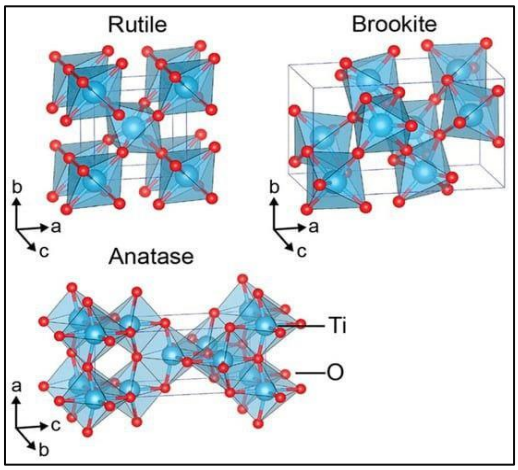


Figure 5. Polymorphs of TiO2 crystal structures:(a) Rutile, (b) Brookite and (c) Anatase [44]

ZrO2 nano particles

Because of their many qualities, nano-ceramics have been used extensively in recent decades to satisfy the demands of many applications.

One of the most well-known ceramic materials is zirconium oxide (ZrO2), commonly referred to as zirconia. It has exceptional physical and chemical qualities, including resistance to abrasion, resistance to high temperatures, strength, toughness, resistance to corrosion, an adjustable expansion coefficient, biocompatibility, and strong chemical properties of oxygen ion conductivity [45].

Zirconium is a strong transition metal that has numerous applications in the form of the oxide, also known as zirconia or zirconium oxide.

For its natural hardness, abrasiveness, high melting point and low resistance to friction, zirconia is sometimes referred to as ceramic steel.Due to its high thermal stability, its exceptional antibacterial, antioxidant and antifungal properties, as well as its high specific area, biocompatibility and chemical stability, it is an ideal material for use in many applications. [46].

Table3:comparative properties of coating materials [1][10][12][40][41][44][45][46] [58][60][63][64].

Property	**Hydroxyapatite**	**Titania**	**Zirconium**
Chemical formula	$Ca(PO_4)_6(OH)_2$	TiO_2	ZrO_2
Crystal structure	Hexagonal unit cell	Rutile Anatase Brookite	Monoclinic tetragonal Cubic (temperature depandance)
Fracture toughness	0.8~1.2 $MPa.m^{1\2}$(brittle)	2.4~3.3MPa.$m^{1\2}$	3.5~5.5MPa.$m^{1\2}$
Compressive strength	500~1000 MPa (dense HA)	500~1500 MPa	2000~3000 MPa
Tensile strength	40~100MPa (significantly lower than bone)	100~200 MPa	200~500MPa
Bioactivity	Excellent osteoconductivity ; promot bone bonding	Good (induces apatite formation in SBF)	Moderate(bio inert ,limited direct bone bonding)
Biocompatibility	Non toxic Non inflammatory Chemically similar to bone mineral	Non toxic Promots osteoblast adhesion	Non toxic Chemically stable
Limitation	Poor mechanical properties: limited to non load bearing applications	Low fracture toughness; Lower bioactivity Compared to HA	Dense structure ; Limited bioactivity; high density; expensive

Critical comparison of HA, TiO_2, and ZrO_2

The comparison presented in Table 3 highlights the complementary characteristics of HA, TiO_2, and ZrO_2. HA provides the highest bioactivity and excellent osteoconductivity because of its chemical similarity to the mineral phase of bone; however, its relatively low tensile strength and fracture toughness indicate an inherent mechanical limitation, particularly under tensile or load-bearing conditions. In contrast, TiO_2 and ZrO_2 exhibit higher fracture toughness and tensile strength than HA, suggesting that their incorporation can provide mechanical reinforcement to HA-based coatings. TiO_2 also offers favorable chemical stability and the ability to promote apatite formation, whereas ZrO_2 provides high strength, toughness, and chemical stability. Therefore, the incorporation of TiO_2 and ZrO_2 should not be considered merely as an increase in coating composition, but rather as a reinforcing strategy intended to balance the high bioactivity of HA with improved mechanical and protective characteristics. However, the effectiveness of such reinforcement depends on factors such as particle distribution, coating composition, and EPD processing conditions, and therefore cannot be assumed to be identical across different studies.

Electrophoretic deposition(EPD)

EPD is a bridge that connects two processes: deposition and electricity[47].

"The EPD process is flexible for the deposition of a range of materials, such as composites, metals, ceramics, glasses and polymers. This option is something that is cost-efficient and doesn't require expensive equipment. Because it is easy to control the shape and thickness of the coatings it generates by precisely modifying process parameters, the EPD is widely used" [48–50].

The main difference between electrochemical deposition (ELD) and electrophoretic deposition (EPD) is that an electric field is used in the latter that contains salts or the positive and negative ions, and in the former an electric field is used that contains suspended particles in a solvent [51].

Cathodic and anodic EPD are the two fundamental kinds of EPD processes. The technique of applying positive charges to the cathode (negative electrode) is called cathodic EPD, the application of negative charges to the anode (positive electrode) is called anodic EPD. As seen in Figure 6 [52].

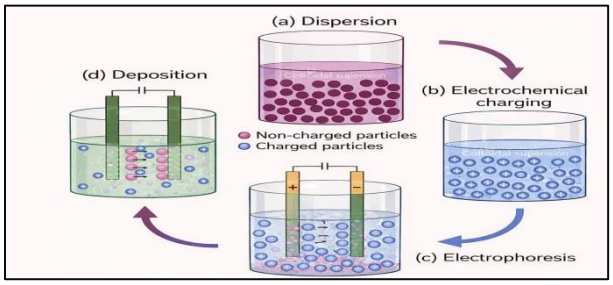


Figure 6. Schematic of the procedure for electrophoretic deposition [52]

Bio coatings effects on bone regeneration ,tissue and biocompatibility of implants

The most important criteria for the selection of the coating material are: (a) sufficient mechanical reliability, adhesion and fracture toughness to resist the applied forces, (b) corrosion resistance in bodily fluid environments, and (c) biocompatibility (without toxicity, inflammation, etc.

A Biomedical coating can be classified into three groups, depending on its efficiency in the organism: bioinert, bioactive, bioresorbable. Bioactive coatings are biomaterials with the ability to release bioactive compounds that help prevent post-operative complications and promote the regeneration of the surrounding tissue and cells around the foreign graft, unlike the bioinert coatings. Absorbable (bio resorbable) coatings are coatings that break down electrochemically in the human body and are then absorbed by the tissue and cells [53–58].

The primary goal of a biocompatible coating is to improve the surface properties of the metal implant with regard to osteoconductivity, osteo-inductivity and osteogenicity. The coating should have osteo-conductive properties, which means that it can serve as a scaffold for the formation of the extracellular bone matrix where osteoblasts can attach and multiply; and it should be osteo-inductive, which means that it stimulates the differentiation of precursor, or stem, cells into osteoblasts. The calcium nodules formed by the osteoblasts join to the collagen matrix of the newly formed bone and harden the collagen matrix [59–63].

TiO2 has a crucial role in biomedical applications owing to its outstanding mechanical properties, antibacterial activity, catalytic activity, and resistance against chemical and photocorrosion. The ability of TiO2 to form calcium phosphate or apatite-like bone on its surface when placed in SBF solution makes it a good candidate for the replacement and reconstruction of bones. Furthermore, it was determined that anodizing TiO2 layer on the surface of Ti substrates is an effective way of lowering the temperature rise during the microwave diathermy treatment and it can be used as an alternative for the rehabilitation of a bone fracture of the inner parts of the body. Tantalum oxide (Ta2O5) is another oxide that could promote the adhesion of soft tissues and bone in a similar manner to TiO2 and be a basis for the formation of apatite that is similar to bone.

The reactive magnetron sputtering technique was used to obtain Tantalum oxide nanocrystals and enhance the corrosion resistance and in vitro biocompatibility of the magnesium alloy at early stages of corrosion. Twin-gun magnetron sputtering coating technique was used to deposit a Ta2O5 coating containing 12.5%Ag, which demonstrated the good activity of killing pathogens such as S. aureus and good cellular biocompatibility with skin fibroblast cells [64–66].

Another important technique to enhance the osteogenic capacity of the oxide coating is grafting of metal ions and compounds, as it has been proven that some metal ions (Ca2+, Sr2+, Mg2+, etc.) can positively influence the osseointegration. The effects of the different metallic ions on the different processes of bone regeneration are illustrated in Figure 7. " [67].

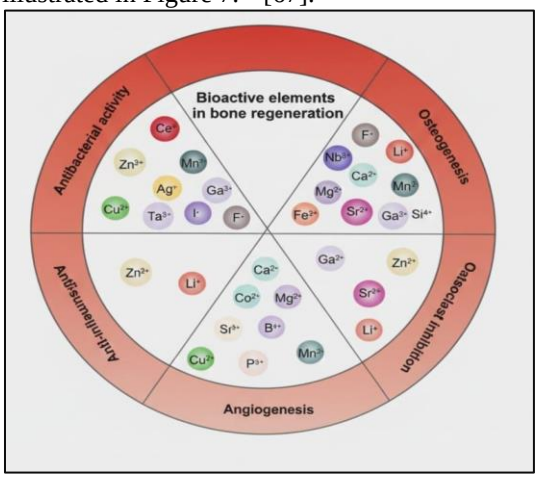


Figure 7. Some ions' therapeutic effects include angiogenic, osteogenic, anti-inflammatory, and antibacterial action [67]

Review Methodology

A systematic literature review was conducted using major scientific databases, including Scopus, ScienceDirect, and Google Scholar. Relevant studies published between 2016 and 2025 were identified using keywords such as hydroxyapatite , EPD , TiO_2 ,ZrO_2,and 316LVM stainless steel. Only peer-reviewed articles focusing on corrosion resistance, mechanical properties, adhesion, and bioactivity of HA-based coatings prepared via electrophoretic deposition were included, while unrelated studies were excluded. Selected papers were critically analyzed and compared to identify key trends and research gaps.

Influence of EPD parameters on coating performance

The performance of EPD-derived HA-based coatings is strongly influenced by the deposition conditions. Deposition voltage and time affect particle transport and the amount of material deposited on the substrate, while suspension characteristics influence the stability and uniformity of the deposited layer. The pH of the suspension can also affect particle charging and dispersion, thereby influencing deposition behavior. In addition, particle size and surface charge, commonly evaluated through zeta potential, are important factors governing suspension stability and particle mobility during EPD. Therefore, differences in these parameters among published studies may contribute to variations in coating morphology, thickness, adhesion, and corrosion performance.

However, the available literature does not provide sufficiently standardized conditions to establish a universal optimum for these parameters. Consequently, the effect of an individual EPD parameter should be interpreted together with the suspension composition, substrate condition, coating formulation, and post-deposition treatment. This highlights the need for systematic optimization and standardized reporting of EPD conditions in future studies, particularly for HA/TiO_2/ZrO_2 coatings on 316LVM stainless steel.

Coating Failure Mechanisms and Stability

Despite the potential benefits of HA-based composite coatings, their long-term stability may be affected by cracking, delamination, and interfacial failure. Residual stresses generated during coating formation, drying, or post-treatment may contribute to crack initiation, while non-uniform deposition or particle agglomeration can introduce defects that weaken the coating. The incorporation of TiO_2 and ZrO_2 may improve the mechanical stability of HA-based coatings, but their effectiveness depends on particle dispersion, coating composition, interfacial bonding, and EPD conditions. Therefore, evaluation of coating integrity should consider not only initial corrosion and adhesion performance but also long-term stability under relevant physiological conditions.

Conclusion

This review highlights the potential of electrophoretic deposition (EPD) for developing HA-based composite coatings on 316LVM stainless steel for biomedical applications. HA provides favorable bioactivity and osteoconductive characteristics, while the incorporation of TiO_2 and ZrO_2 can provide complementary mechanical and protective functions. However, the performance of these composite coatings is strongly dependent on coating composition, suspension characteristics, deposition conditions, interfacial bonding, and post-deposition treatment.

The reviewed literature also indicates that direct comparison among reported coating systems remains difficult because of variations in substrate preparation, EPD parameters, coating formulations, and testing procedures. In addition, the inconsistent reporting of quantitative performance indicators limits the establishment of a universal optimum coating composition or deposition condition. Coating cracking, delamination, residual stresses, particle agglomeration, and long-term stability therefore remain important issues requiring further investigation.

Future research should focus on systematic optimization of HA/TiO_2/ZrO_2 composition and EPD parameters, standardized reporting of coating characteristics and performance indicators, and comprehensive evaluation of corrosion, adhesion, mechanical behavior, and bioactivity. Long-term immersion and biological studies are also required to clarify coating stability and support the potential translation of these composite coatings toward biomedical applications.

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