



REVIEW

Different Coating Methods of Titanium Dioxide on Metal Substrates for Orthopedic and Dental Applications: A Review

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The outstanding physico-chemical characteristics to assist bone regeneration and cell development, titanium dioxide (TiO₂) based materials have showed significant promise for applications in implants. Due to its excellent performance in a wide variety of applications, chemical stability, and inexpensive cost, this metal oxide has received the more attention. Coating techniques for creating surfaces made of this substance have been thoroughly investigated. The aim of this review article is to look at the current status of TiO₂ technology for orthopedic and dental implants. Over the years, researchers have investigated several TiO₂ coating deposition techniques on metal implants, with the goal of improving adhesion strength and long-term dependability. This review examines a variety of TiO₂ deposition techniques on metal substrates in depth. Anodization, sol-gel method, plasma spray coating, cold spray coating, high velocity oxy-fuel spray, high velocity suspension flame spraying, pulsed laser deposition (PLD), ion beam deposition (IBD), magnetron sputtering deposition, electrophoretic deposition (EPD), electrochemical deposition and biomimetic deposition are among the methods examined.

Keywords: Titanium dioxide, Coating deposition techniques, Cold spray, High velocity oxy-fuel spray, Anodization.

INTRODUCTION

Biomaterials are new composite materials which are used to replace or support an organ or tissue, and they must be biocompatible even though they bring within full contact with biological systems [1]. Biomaterials are divided into four groups depending on their medicinal use. First-generation biomaterials are inert biomaterials that have been developed and selected since 1950 to aid in the repair or replacement of host tissue while causing no adverse reactions in the biological system. Cobalt alloys, alumina and stable polyurethane were among several, but they were vital in orthopaedic and dental applications [2]. Second-generation biomaterials with bioactive or biodegradable qualities have been studied since 1970. Second generation biomaterials such as titanium and calcium phosphates or hydroxyapatite, have shown low durability over time. Further research is focused on creating impermanent materials that must be degraded in a controllable way through duration while still fostering natural integration of the graft with the

bone it will eventually replace, such as magnesium and its alloys [3]. By year 2010, researchers started testing a new generation of biomaterials, particularly involves biomimetic nanocomposites for tissue engineering applications [4,5].

Biomaterial science is mainly reliant on implant development and improving the replacement or repair method. The implant diminishes after healing and is removed by host tissues. Metal alloys based on titanium, stainless steel 316L, nickel-titanium, magnesium and cobalt are widely used as prosthetic devices [6]. Their high mechanical strength, wear resistance, and corrosion resistance are the reasons for using these metal alloys. These implants should be used to preserve the bones in place and assist in osseointegration with the overlying bone tissue. Implants used to strengthen tissue must be biocompatible and also provide clues to host cells in order to trigger a cellular repair process [7]. Coatings on biomedical implants are deemed to be a promising solution to grow implant-tissue interactions and boost biocompatibility and biofunctionality without disrupting the material's properties [8,9].

Titanium dioxide, commonly known as titanium(IV) oxide or titania [10], is a naturally occurring white solid with a variety of properties, including low modulus of elasticity, high tensile strength, biocompatibility and corrosion resistance, as well as extensive uses [11-14]. Rutile, anatase and brookite are the three natural polymorphic forms of TiO₂ [15,16]. A deformed octahedron [17,18] is produced when a Ti⁴⁺ cation is coordinated by six-oxygen atoms. The polymorphic topologies of these octahedrons are determined by the way they assemble. The rutile form has a tetragonal structure with two TiO₂ molecules in each unit cell, whereas the anatase form has a tetragonal structure with four TiO₂ molecules in each unit cell. Brookite is the least dense TiO₂ form, with an orthorhombic structure and an eight-molecule unit cell, as compared to anatase and rutile [19,20]. Depending on its polymorphic phase, TiO₂ exhibits distinct properties. At high temperatures, anatase and brookite can be permanently converted to rutile, although rutile is the most stable phase.

Because of its potential uses in science and technology, TiO₂ has received great of interest in recent years [21-27]. TiO₂ has a big future for usage in bone and dental implants with its mechanical qualities, biocompatibility, low cytotoxicity, bodily fluid stability and corrosion resistance [21-26]. TiO₂ evokes a strong molecular response and osseointegration, leading to improved bone strength [28,29]. TiO₂ can be used as a covering for metallic implants in tissue engineering applications. Surface alteration, such as a thicker TiO₂ coating on the metal surface, can help titanium to osseointegrate better [30-32]. TiO₂ coatings on metallic surfaces have been demonstrated to increase corrosion resistance, biocompatibility, cell efficiency and even bone formation [33,34]. Studies have shown that TiO₂ coatings increase mechanical resistance, osseointegration, cell fixation, bone strength and corrosion resistance because hydroxyapatite is comparable to many calcified tissues of vertebrates [35-40]. An effort to introduce TiO₂ physiological and morphological consistent. Titanium dioxide coatings are used in biomedical engineering for dentistry and orthopaedic applications due to their mechanical qualities and biocompatibility [41-44]. TiO₂ has been used as a protective coating on titanium substrates, 316L stainless steel and other metals [45,46].

Because of its excellent chemical stability and non-toxic nature, TiO₂ coating plays an important role in various fields of research and may lead to attractive characteristics. TiO₂ has been explored for a variety of possible functions including as a coating for biomaterials [47,48] and as a corrosion-resistant material [49-53]. Plasma spray coating, cold spray coating, high velocity oxy-fuel spray, high velocity suspension flame spraying, pulsed laser deposition (PLD), ion beam deposition (IBD) and magnetron sputtering deposition are all examples of anodization. Excellent adhesion, fast deposition rates, and great control over the metal substrate are some of the benefits of electrophoretic deposition (EPD), electrochemical deposition and biomimetic deposition. As a result, the purpose of this work is to analyze and looked into its viability of TiO₂ coating methods for bone and dental implants, since there are many published articles available in the literature from the past year 1994 to till 2021.

Titanium dioxide coating methods: TiO₂ coating on metal implants can be carried out by several methods. Coating methods, on the other hand, are beneficial in certain applications based on the morphology, productivity, compatibility, stability and functionality desired. Different deposition mechanisms for TiO₂ coating systems must be researched in order to reveal their benefits and drawbacks for the target application. Anodization, sol-gel, thermal spray, physical vapour deposition (PVD), chemical vapour deposition (CVD) and electrodeposition are among the many coating processes available, but just a few are among the most effective and adaptable. Low-temperature thermal processes for TiO₂ coatings, which is rare to find has been developed on metal substrate are reliable and repeatable.

(A) Anodization: When an electric field is placed between a metal and an anode, ionic diffusion occurs, resulting in the formation of controlled nanotubes on the anode surface. The procedure is carried out when a two-electrode system is subjected to alternating voltage in an electrolyte under controlled circumstances [54]. TiO₂ nanotubes may be made using acidic aqueous hydrogen fluoride electrolytes or neutral solutions containing fluoride salts [55]. The voltage employed in the anodization process changes the diameter of TiO₂ nanotubes. Several researchers have demonstrated that changing the applied voltage may change the diameters of TiO₂ nanotubes and that the kind of electrolyte used in the anodization process can also affect the diameters [56,57]. In an early work, titanium metal sheet was utilized to generate nanotubes using NH₄F and H₃PO₄ electrolytes, respectively and on changing the electrolyte from fluoride to phosphate, increased the nanotube diameter from 174.2 to 235.3 nm [58,59].

(B) Sol-gel method: Because it generates low-cost coatings with high adherence and permits structural control, the sol-gel technique is a viable alternative method for coating diverse metal substrates [60]. The process begins with the creation of a colloidal suspension of a molecular precursor in a solvent (sol), which is then followed by the production of an oxide network at low temperatures. Two steps of the process include the hydrolysis and condensation of the suspension, as well as a polycondensation reaction that results in a three-dimensional network. A room-temperature drying cycle (ageing) is then used to remove the solvent from the gel, followed by a heat treatment to create monoliths or thin films. The sol-gel transition is influenced by the quantity of precursors, water, catalyst, temperature and pH [61]. Several researchers have used the sol-gel technique to create TiO₂ coatings. Wang *et al.* [62] devised a novel technique of dip and spin coating using sol-gel to produce ultrafine TiO₂ films on α -Al₂O₃ discs. The process was unique in that it submerged the substrate in the sol first, then withdrew it to spin a thin coating, resulting in tiny glass films with homogeneous grains and structure. The scientists claim that the surface modification with TiO₂ *via* sol-gel can enhance protein adsorption *in vitro* due to changes in surface chemical composition, roughness, and wettability. Sol-gel was utilized by Advincula *et al.* to illustrate the physiological response of TiO₂ on metal surfaces, revealing an increase in cell adhesion, cellular responsiveness, and matrix mineralization [63-65]. Furthermore, it has been shown in the literature that sol-gel

TiO₂ can induce the formation of calcium phosphates on TiO₂ surfaces, therefore, increasing cell attraction to biological tissue [66]. Guo *et al.* [67] reported that a porous TiO₂ coating made using the sol-gel technique has a biocidal effect. Fu *et al.* [68] discovered a biocidal effect when using sol-gel TiO₂ coatings on glass substrates. The antibacterial property of TiO₂ have been researched extensively, and the biological mechanism by which this occurs is now being explored [69].

(C) Thermal spray method: Because of their hardness, biocompatibility, wear and corrosion resistance, thermal spraying is commonly employed to create TiO₂ coatings for biomedical applications [70]. Thermal spray approach has been shown to be successful in obtaining TiO₂ coatings with effective biological performance [71]. Thermal spraying involves spraying the coating material (usually a powder with a particle size distribution ranging from 10 to 100 nm) into an enthalpic source, such as a thermal or flame created by ionization-excitation of inert gases or combustion. The particles are heated or partially melted before being crushed on the target substrate, where they quickly solidify and deposit.

(D) Plasma spray coating: Coating works by either permeating the substrate or deforming the particles as a result of the energy impact. In the latter scenario, after a succession of sprayings, the flattened particles collect and cover the substrate's surface; moreover, this procedure is capable of holding various atmospheric protections, such as air, inert gas or vacuum [72]. Even though it may deposit metallic alloys, oxides and ceramics, plasma spray coating is one of the most researched techniques of material deposition and it has a wide range of applications in biomaterial and body implant coatings [73,74]. The results of high velocity oxygen fuel (HVOF) and high-velocity suspension flame spraying (HVSFS) coatings are equivalent to this technique. Composite coating materials with a flow of solid particles incorporated into a heated and accelerated plasma stream are possible due to the high temperature of this method. The plasma jet has been reported to reach temperatures of 10,000 K or more, however after it leaves the nozzle tip, the temperature drops significantly [75]. Plasma-treated surfaces exhibit high coating adhesion [76] and coating thicknesses of 25-100 nm have no detrimental impact, but increasing the thickness to 150 nm reduces the mechanical part's wear performance. The thickness of the coating layer, according to the findings, increases the material difference between the substrate and the coating layer. Excessive heat stress to the substrate during thicker coating development, on the other hand, creates tiny fractures in both the coating layer and the substrate, reducing the component's fatigue life.

(E) Cold spray coating: Cold spraying is a method in which powder particles (ranging in size from 5 to 100 nm) are designed to obtain a coating on a suitable substrate via ballistic impingement. The solid particles deform and create a link with the substrate after being accelerated by injecting them into a high-velocity gas stream and smashing them on it [77]. When solid particles are sprayed onto a substrate, a variety of phenomena on the substrate surface are seen in proportion to process variables such as substrate hardness, ductility, velocity size, incidence angle and so on. Despite the fact that particles can

be submerged in the surface by a deposition process if the velocity is high enough, substrate characteristics like as hardness, temperature, and degree of oxidation play an important influence in particle-substrate bonding [78-80].

The bonding process of TiO₂ particles cold-sprayed onto metal and ceramic surfaces has been widely explored. Winnicki *et al.* [81] employed a low-pressure cold-spray technique to make amorphous, anatase and rutile TiO₂ powders with particle sizes of 10-70 nm. The TiO₂ coatings were made on aluminium, and the powder deposition mechanism was mechanical interlocking of microscopic particles with a local presence of agglomerates, showing that the working gas temperature was the most important element in the process. To test the binding strength of the coating, Schmidt *et al.* [82] used 0.1-10 nm TiO₂ particles that were cold sprayed thoroughly over a good surface of the titanium substrate, as well as ultrasonic cleaning with a maximum intensity of 40.8 W cm⁻². Kliemann *et al.* [83] utilized 3-50 nm TiO₂ agglomerates to cover steel, Cu, Ti and AlMg₃ surfaces continuously, identifying the bendable substrates that allow for shear instabilities as the primary adhesion between the particles and the substrate as the primary adhesion between the particles and the substrate. The impact morphology of single TiO₂ particles as well as examined deposition of different particles on substrates at various temperatures was assessed by Hajipour *et al.* [84]. Only when the substrate temperature exceeded a particular threshold could a single TiO₂ particle be deposited. It has been hypothesized that preheating the substrates softens them and encourages substrate shear instability, allowing for easier coating deposit. The chemical connection between the particles and the substrate is responsible for the deposition of TiO₂ on substrate in the cold-spraying method. The fact that films of titanium suboxide provide the substrate with the appropriate surface roughness for the TiO₂ particle suggests that substrate hardness may enhance particle-substrate interaction. Hussain *et al.* [85] used TiO₂ coatings of 400 and 150 microns on metal and tiles, respectively. The adhesion strength of TiO₂ coatings was found to be impacted by the substrate's hardness and oxidizability, which may be improved by changing the substrate's surface. It was also suggested that preheating might increase oxidizability while reducing the coated substrate's adhesive strength. The TiO₂ particle deposition was improved by pre-heating the substrate, according to Gutzmann's experiment.

(F) High velocity oxy-fuel (HVOF) spraying: Before entering an internal combustion chamber, a gaseous or liquid fuel is pre-mixed with oxygen at isothermal conditions and flow rates, the oxy-fuel mixture is continuously ignited and the combustion products are forced along the gun barrel nozzle to produce a supersonic flame in high velocity oxy-fuel (HVOF) thermal spraying. A convergent-divergent nozzle is often employed in liquid-fueled HVOF guns, which provides better gas flow acceleration and high powder particle momentum yield [86]. Powder is generally delivered into the hot gas stream downstream of the nozzle rather than immediately into combustion chambers, reducing powder particle overheating. Liquid fuels, such as kerosene, are particularly difficult to burn due to the broad variety of composition and fuel quality. Changing the

gas fluxes and mixing ratios, or the ratio of fuel to oxygen, will change the temperature and velocity of the flame [87]. Because the powder particles contact the substrate at a high speed, resulting in dense coatings, HVOF thermal spray is an effective technique for applying nanostructured material coatings. The low gas temperature prevents particles from becoming superheated during flight, allowing powders placed on the substrate to maintain their nanocrystalline structure [88]. Thermal spray can be utilized to create TiO₂ coatings that decompose organic molecules, according to recent study [89]. Thermal spray techniques can cause anatase to convert into rutile due to the heat produced in the particle during the spray [90]. As a result of this consequence, spray coatings often include more rutile, which has poor photocatalytic capabilities [91]. It was claimed that a coating with an anatase content of 12.6% and 55% by volume could be deposited using gas fuel and HVOF spraying of anatase TiO₂ [92].

(G) High-velocity suspension flame spraying: To achieve consistency, a high-velocity suspension flame spraying (HVSFS) technique is used to coat suspensions with a spray mechanism [93]. Many difficulties encounter due to the handling of suspensions, but this problem can be resolved by using axial powder injection. In this process, HVSFS covers the injection complications and obtained coatings are very dense and uniform with this technique [94]. The main feature includes lower cost with high efficiency along with no post-treatment requirements and yields better coatings with uniform structure when the desired thickness is less than 50 μm [95-99]. The higher thickness of coating lead to decrease the mechanical properties along with adhesive bonding of coating with the metal surface. Stresses also started to generate on the metallic surface due to the thick coating. As a result of the breakdown of the protective oxide covering, metallic ions are ejected as a result of corrosion of the metallic surface [100]. The suspension was injected axially in the HVSFS case to avoid intense flame interruptions producing instabilities in the spray process [101]. According to the XRD measurements, Gadow *et al.* [102] successfully deposited TiO₂, with anatase accounting for roughly 75% of the coating and rutile accounting for the rest. A full mechanical assessment of the samples was also performed, as well as the application of HVSFS nano-TiO₂ coatings for substrates.

(H) Vapour deposition method: Vapour deposition methods are coating procedures that use condensation, chemical reactions or conversion to condense materials in a vapour state in order to produce thin films on diverse surfaces. There are two types of vapour deposition technologies: (i) physical vapour deposition (CVD) and (ii) chemical vapour deposition (PVD).

(i) Physical vapour deposition (PVD): It is a flexible coating technique which includes vaporising solid metal in a high vacuum and depositing it on insulating systems. It is considered ecologically friendly since it allows for the deposition of all inorganic and organic elements, as well as certain organic compounds, and it has a good corrosion resistance. Brohede *et al.* [103] used PVD to generate a bioactive anatase TiO₂ composition and an adhesion-enhancing gradient layer on the surface. PVD is a coating technique that entails vapourizing solid metal in a high vacuum and depositing it on metallic

surfaces. On the other hand, coating complex forms remains a substantial disadvantage.

(a) Pulsed-laser deposition: The pulsed-laser deposition (PLD) process involves ablation and crystallization of a target material on the substrate's surface using a laser. Ion beam deposition and magnetron sputtering are employed in the PVD of TiO₂ coatings. The discovery of crystalline anatase and rutile like structures in TiO₂ coatings of PLD was revealed by several scientists [104]. The process of depositing TiO₂ coatings with PLD is poorly understood and documented. These structures are analogous to two additional PVD TiO₂ coatings dependent on the deposited species' substrate: high temperatures and energies favour rutile growth, whereas low temperatures and energies favours anatase and amorphous films [105]. In most PVD processes, high substrate temperatures are necessary for good coating adherence and deep coating structures prevent heat-sensitive substrates like pre-quenched tools or polymer materials from being coated. The PLD technique is a well-developed scientific deposition process that permits the coating of these materials at room temperature with excellent adhesion strength due to the high ionized vapour (plasma) ablated from the target by the laser beam [106].

(b) Ion-beam deposition: Ion beam deposition techniques are used to deposit TiO₂ in a number of applications [107]. Since the mid-1970s, many ions bombardment-based surface modification technologies have been developed and are widely used to change the surface of metals, polymers, ceramics and biocompatible materials, including ion beam aided deposition (IBAD), ion beam assisted deposition and ion mixing. Ion beam aided deposition (IBAD) is a vacuum-based PVD and ion beam bombardment technique [108]. The bombardment of the coating with a high-energy ion beam during deposition is the key characteristic of IBAD. Several factors impact the composition, structural, mechanical and chemical characteristics of the as-deposited coating in the IBAD process, with ion bombardment remaining the most significant [109]. The most significant processing requirements are coating materials, evaporation rate or sputtering rate, ion species, ion energy and ion beam current density. IBAD's capacity to generate biocompatible coatings with substantially higher substrate adhesive strength than traditional coating techniques is one of its most attractive characteristics [110]. The consequence of ion bombardment-assisted interaction between the coating and substrate atoms, resulting in an atomic intermixed zone at the coating-substrate interface, is considered to be this. It also has a low substrate temperature as well as high reliability and repeatability, all without sacrificing physicochemical properties. Another interesting feature of the IBAD technique is its better control over coating microstructure and chemical makeup [111,112].

(c) Magnetron sputtering deposition: The physical vapour deposition, particularly magnetron sputtering, is frequently suggested as a preferred approach for fabricating photocatalytic TiO₂ films [113-115]. Over chemical deposition techniques, magnetron sputtering provides a number of benefits, including coating uniformity over large areas, exceptional control over chemical and morphological characteristics of the films, the lack of poisonous or dangerous precursors, and significant

extensibility [116]. Based on particular studies, magnetron sputtering also has the advantage of providing longer lasting titanium dioxide films than sol-gel methods. Magnetron sputtering is frequently utilized in the industrial production of commercially accessible photocatalytic goods [117]. The bombardment of a negatively biased solid target with positively charged ions (typically argon) produced in a glow discharge plasma, followed by the condensation of the target atoms on the substrate to form a thin layer, is known as magnetron sputtering [118]. In magnetron sputtering, strong ions from a noble gas are used to sputter titanium (Ti) from a metallic target. By supplying a reactive gas to the chamber, TiO₂ may be generated and deposited on a specific substrate. Mild steel deposition is very energy-dependent and deposition of crystalline TiO₂, particularly in the rutile phase, generally necessitates either a substrate bias voltage, a very high substrate temperature or a combination of both [119].

(ii) Chemical vapour deposition (CVD): Chemical vapour deposition is a chemical process that occurs when gaseous reactants come into contact with a heated surface (CVD). A highly controlled coating is achieved both quantitatively (high purity with fine control of chemical product deposition) and qualitatively (surface topography, number of layers) (high purity with fine control of chemical product deposition). This typical method has shown to be quite useful in biological applications. Goikhman *et al.* [120] effectively demonstrated that TiO₂ coating exhibited significant photocatalytic antibacterial activity against *E. coli* under visible light, with a 30% survival rate after 3 h. Xu *et al.* [121] suggested a one-step CVD method for depositing a tiny quantity of graphitic C₃N₄ on aligned TiO₂ nanotube layers. CVD was also used to apply single-layer graphene sheets on titanium discs. The scientists ingeniously demonstrated that a heat treatment (2 h at 160 °C) enhanced graphene adherence to titanium while having no detrimental effect on antibacterial activity.

(I) Electrodeposition coating: Electrodeposition is a protective method that involves depositing metallic ions on a substrate. In this reaction, ion transport is induced by a potential difference between the anode and cathode poles. Extensive studies have been done on electrodeposition coating by accepting ions from the other electrode, a coating layer forms on the submerged sample after a period [122]. Electrochemical deposition (ECD) and electrophoretic deposition (EPD) are the two forms of electrodeposition coating processes in general.

(i) Electrophoretic deposition: The electrophoretic deposition (EPD) technique, which utilizes the movement of charged particles in an electrolytic solution, has been extensively studied. The ceramic particles are charged by an electric field in an aqueous or non-aqueous liquid. Deposition of thin films on the surface of an implantable material enhances the strength and corrosion resistance of metal implants when the protection given by the original surface oxide layer is insufficient. The suspension in an EPD is made up of powder particles which are randomly dispersed in an aqueous or non-aqueous solution, as well as the anode and cathode electrodes. Positively charged suspended particles will settle in the cathodic compartment, whereas negatively charged particles will drift toward

the anode. Besra & Liu [123] investigated the suspension composition as well as the processing factors that impact electrophoretic deposition. Particle size, dielectric constant, conductivity and zeta potential influence the quality of the suspension, whereas voltage, deposition duration and substrate conductivity determine the effectiveness of EPD deposition. Lower surface charged particles attract one another, resulting in a porous deposited coating, whereas higher surface charged particles create a strong electrostatic repulsion force during deposition, resulting in a thick coating. As a result, a homogeneous particle suspension with a medium dielectric constant and adequate conductivity results in improved deposition.

(ii) Electrochemical deposition: In the electrochemical coating process, substrates go through a series of electrochemical stages before being effectively coated. In this technique, the potential difference between the cathodic and anodic poles of an electrical circuit is exploited to generate micro-arcs or to transfer ions between the anion and cation sides [124]. The two stages of the surface coating are electrophoretic and electrolytic depositions. The first is in charge of depositing large suspension particles found inside the electrolyte, while the second is in charge of depositing fine materials and structure. These two techniques can be seen as separate processes or as components of a larger coating process [125,126]. Electrochemical methods dissolve desired coating ingredients in the working electrolyte. On Ti and Ti alloy surfaces, the most electro-deposition coatings have been applied [127]. One of the characteristics of electrochemical coatings is the thickness uniformity of the deposited layer across the substrate [128,129]. Zhao *et al.* [130] investigated the use of platinum and graphite anodic electrodes and discovered that they enhanced coating quality and increased deposition rate. Despite the fact that it is a low-temperature technique, the coated substrates must go through a series of densification and sintering stages in the furnace. The surface of the coated substrate is not a compact structure due to the large suspension particle deposition during the electrophoretic process [130]. Sharp edges, such as microcracks, are more prone to ion exchange due to electrochemical factors, and as a result, material deposition occurs at a quicker pace. This characteristic guarantees that the coating layers are as uniform as possible [131].

(J) Biomimetic deposition: This method constitutes of mimicking natural building processes of bone. In this way, hydroxyapatite can be used to enhance the osseointegration of natural bone and coated artificial implant [132]. The biomimetic coating process matches the capabilities of actual bone tissues; it encourages osteoblast cell adhesion and growth. The presence of hydroxyl groups on the surface of the implant is required for a biomimetic technique, just as it is for other chemical coating methods. This functional group can easily attach to the acid or alkali pre-treatment stage. These functional groups on the substrate surface facilitated in the creation of apatite by encouraging CaP nucleation and following crystallization. The biomimetic coating processes were place under normal pH and temperature ranges [133,134].

Amorphous and crystalline TiO₂ gels were used to study the production of hydroxyapatite submerged in simulated body

fluid (SBF) [135]. In simulated body fluid, amorphous TiO₂ gels did not stimulate hydroxyapatite production on their surfaces, but anatase or mixed anatase-rutile gels did. The effect of doping elements on the sol-gel technique has also been explored [136]. TiO₂ gels with an amorphous structure did not induce the production of hydroxyapatite on their surfaces in simulated body fluid, whereas gels with anatase or mixed anatase-rutile did [137]. Few researches also investigated the effect of doping drugs on the sol-gel method [138]. They reported that the adding calcium ions to TiO₂ surfaces increases bio-activity and enhances hydroxyapatite formation. For biomimetic apatite synthesis on materials, chemical species for nucleation induction should be added to the surfaces. A rise in apatite mass transfer affects formation in simulated bodily fluid (SBF) [139,140]. The apatite is not formed biomimetically on a single crystal TiO₂ (anatase). SBF has a propensity to absorb water at the surface due to the buildup of titanium hydroxide groups of TiO₂. Titanium hydroxide groups are scarce in the thickness at the surface, according to Li *et al.* [141]. The nucleation and crystallization of apatite is triggered by these groups. They create apatite, which looks like bone.

Conclusion

This review article presents an overview on different coating methods of TiO₂ on metal substrates. In biomaterials research and biomedical engineering, TiO₂ surface coating methods are crucial. Biocompatibility can be improved and difficulties associated with metal substrate deterioration can be avoided by applying a TiO₂ surface coating while retaining bulk characteristics. As a result, this review discusses the TiO₂ coating techniques used to increase the biological and corrosion resistance of metal substrates. Anodization, sol-gel and electrodeposition coatings have proved to be desirable owing to their low processing costs and ability to create homogeneous surfaces, which minimize surface roughness on implants. Biological responses can be regulated by altering fabrication methods and applying heat treatments. The corrosion resistance and biological characteristics of the bone implant interface of metal substrates can be selectively strengthened *via* appropriate surface treatments. TiO₂ coatings have shown to be attractive because surface treatments with innovative and creative materials can reduce the rate of corrosion and promote absorption between the bone and the implant.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- Q. Chen and G.A. Thouas, *Mater. Sci. Eng. Rep.*, **87**, 1 (2015); <https://doi.org/10.1016/j.mser.2014.10.001>
- D.F. Williams, *Biomaterials*, **29**, 2941 (2008); <https://doi.org/10.1016/j.biomaterials.2008.04.023>
- W. Elshahawy, eds.: C. Sikalidis, Biocompatibility, In: Advances in Ceramics - Electric and Magnetic Ceramics, Bioceramics, Ceramics and Environment, Chapt. 15, InTech (2011); <https://doi.org/10.5772/726>
- R. Murugan and S. Ramakrishna, *Compos. Sci. Technol.*, **65**, 2385 (2005); <https://doi.org/10.1016/j.compscitech.2005.07.022>
- B. Allo, D. Costa, S. Dixon, K. Mequanint and A. Rizkalla, *J. Funct. Biomater.*, **3**, 432 (2012); <https://doi.org/10.3390/jfb3020432>
- B. Richards, *Sol. Energy Mater. Sol. Cells*, **79**, 369 (2003); [https://doi.org/10.1016/S0927-0248\(02\)00473-7](https://doi.org/10.1016/S0927-0248(02)00473-7)
- K. Alvarez and H. Nakajima, *Materials*, **2**, 790 (2009); <https://doi.org/10.3390/ma2030790>
- X.Q. Zhang, L.H. Yin, T. Tang and Y.P. Pu, *Biomed. Environ. Sci.*, **24**, 661 (2011); <https://doi.org/10.3967/0895-3988.2011.06.011>
- G. Shen, Y. Chen, L. Lin, C. Lin and D. Scantlebury, *Electrochim. Acta*, **50**, 5083 (2005); <https://doi.org/10.1016/j.electacta.2005.04.048>
- S. Jafari, B. Mahyad, H. Hashemzadeh, S. Janfaza, T. Gholikhani and L. Tayebi, *Int. J. Nanomed.*, **15**, 3447 (2020); <https://doi.org/10.2147/IJN.S249441>
- Z.N. Jameel, A.J. Haider, S.Y. Taha, S. Gangopadhyay and S. Bok, *AIP Conf. Proc.*, **1758**, 020001 (2016); <https://doi.org/10.1063/1.4959377>
- J. Feng, X. Yan, K. Lin, S. Wang, J. Luo and Y. Wu, *Mater. Lett.*, **214**, 178 (2018); <https://doi.org/10.1016/j.matlet.2017.12.005>
- I.E. Shepa, E. Mudra, M. Vojtko, P. Tatarko, V. Girman, O. Milkovic, T. Sopcak, V. Medvecka and J. Dusza, *Ceram. Int.*, **44**, 17925 (2018); <https://doi.org/10.1016/j.ceramint.2018.06.268>
- M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S. Dunlop, J.W. Hamilton, J.A. Byrne, K. O'Shea, M.H. Entezari and D.D. Dionysiou, *Appl. Catal. B*, **125**, 331 (2012); <https://doi.org/10.1016/j.apcatb.2012.05.036>
- A.J. Haider, R.H. Al-Anbari, G.R. Kadhim and C.T. Salame, *Energy Procedia*, **119**, 332 (2017); <https://doi.org/10.1016/j.egypro.2017.07.117>
- Y. Li, J. Luo, X. Hu, X. Wang, J. Liang and K. Yu, *J. Alloys Compd.*, **651**, 685 (2015); <https://doi.org/10.1016/j.jallcom.2015.08.168>
- P. Roy, S. Berger and P. Schmuki, *Angew. Chem. Int. Ed.*, **50**, 2904 (2011); <https://doi.org/10.1002/anie.201001374>
- B. Sarkar, N. Singhal, R. Goyal, A. Bordoloi, L.N. Sivakumar Konathala, U. Kumar and R. Bal, *Catal. Commun.*, **74**, 43 (2016); <https://doi.org/10.1016/j.catcom.2015.10.035>
- S. Shen, J. Chen, M. Wang, X. Sheng, X. Chen, X. Feng and S.S. Mao, *Prog. Mater. Sci.*, **98**, 299 (2018); <https://doi.org/10.1016/j.pmatsci.2018.07.006>
- J. Singh, S.A. Khan, J. Shah, R. Kotnala and S. Mohapatra, *Appl. Surf. Sci.*, **422**, 953 (2017); <https://doi.org/10.1016/j.apsusc.2017.06.068>
- T. Tao, I.T. Bae, K.B. Woodruff, K. Sauer and J. Cho, *Ceram. Int.*, **45**, 23216 (2019); <https://doi.org/10.1016/j.ceramint.2019.08.017>
- X. Chen and A. Selloni, *Chem. Rev.*, **114**, 9281 (2014); <https://doi.org/10.1021/cr500422r>
- G. Fostad, B. Hafell, A. Førde, R. Dittmann, R. Sabetrasekh, J. Will, J. Ellingsen, S. Lyngstadaas and J. Haugen, *Eur. Ceram. Soc.*, **29**, 2773 (2009); <https://doi.org/10.1016/j.jeurceramsoc.2009.03.017>
- H. Haugen, J. Will, A. Köhler, U. Hopfner, J. Aigner and E. Wintermantel, *J. Eur. Ceram. Soc.*, **24**, 661 (2004); [https://doi.org/10.1016/S0955-2219\(03\)00255-3](https://doi.org/10.1016/S0955-2219(03)00255-3)
- T. Kasuga, H. Kondo and M. Nogami, *J. Cryst. Growth*, **235**, 235 (2002); [https://doi.org/10.1016/S0022-0248\(01\)01782-1](https://doi.org/10.1016/S0022-0248(01)01782-1)
- K. Lee, A. Mazare and P. Schmuki, *Chem. Rev.*, **114**, 9385 (2014); <https://doi.org/10.1021/cr500061m>
- H. Nygren, P. Tengvall and I. Lundström, *J. Biomed. Mater. Res.*, **34**, 487 (1997); [https://doi.org/10.1002/\(SICI\)1097-4636\(19970315\)34:4<487::AID-JBM9>3.0.CO;2-G](https://doi.org/10.1002/(SICI)1097-4636(19970315)34:4<487::AID-JBM9>3.0.CO;2-G)
- Y. Fu and A. Mo, *Nanoscale Res. Lett.*, **13**, 187 (2018); <https://doi.org/10.1186/s11671-018-2597-z>

29. M. Garcia-Lobato, A. Mtz-Enriquez, C. Garcia, M. Velazquez-Manzanares, F. Avalos-Belmontes, R. Ramos-Gonzalez and L. Garcia-Cerda, *Appl. Surf. Sci.*, **484**, 975 (2019); <https://doi.org/10.1016/j.apsusc.2019.04.108>
30. N.K. Awad, S.L. Edwards and Y.S. Morsi, *Mater. Sci. Eng. C*, **76**, 1401 (2017); <https://doi.org/10.1016/j.msec.2017.02.150>
31. L.M. Bjursten, L. Rasmusson, S. Oh, G.C. Smith, K.S. Brammer and S. Jin, *J. Biomed. Mater. Res. A*, **92**, 1218 (2010); <https://doi.org/10.1002/jbm.a.32463>
32. S.M.F. Gad El-Rab, S.A. Fadlallah and A.A. Montser, *Appl. Surf. Sci.*, **261**, 1 (2012); <https://doi.org/10.1016/j.apsusc.2012.05.139>
33. A. Bandyopadhyay, A. Shivaram, I. Mitra and S. Bose, *Acta Biomater.*, **96**, 686 (2019); <https://doi.org/10.1016/j.actbio.2019.07.028>
34. K. Cowden, M.F. Dias-Netipanyj and K.C. Papat, *Nanomedicine (Lond.)*, **17**, 380 (2019); <https://doi.org/10.1016/j.nano.2019.01.008>
35. F. Visentin, A. Galenda, M. Fabrizio, S. Battiston, N. Brianese, R. Gerbasi, V. Zin and N. El Habra, *Appl. Surf. Sci.*, **490**, 568 (2019); <https://doi.org/10.1016/j.apsusc.2019.06.067>
36. T. Wang, Z. Weng, X. Liu, K.W. Yeung, H. Pan and S. Wu, *Bioact. Mater.*, **2**, 44 (2017); <https://doi.org/10.1016/j.bioactmat.2017.02.001>
37. M. Enayati-Jazi, M. Solati-Hashjin, A. Nemati and F. Bakhshi, *Superlattices Microstruct.*, **51**, 877 (2012); <https://doi.org/10.1016/j.spmi.2012.02.013>
38. A.E. Hannora and S. Ataya, *J. Alloys Compd.*, **658**, 222 (2016); <https://doi.org/10.1016/j.jallcom.2015.10.240>
39. H.W. Kim, Y.H. Koh, L.H. Li, S. Lee and H.E. Kim, *Biomaterials*, **25**, 2533 (2004); <https://doi.org/10.1016/j.biomaterials.2003.09.041>
40. Anushika, P. Sharma, A. Trivedi and H. Begam, *Mater. Today Proc.*, **16**, 302 (2019); <https://doi.org/10.1016/j.matpr.2019.05.094>
41. C. Frandsen, K. Noh, K. Brammer, G. Johnston and S. Jin, *Mater. Sci. Eng. C*, **33**, 2752 (2013); <https://doi.org/10.1016/j.msec.2013.02.045>
42. L. Bao, J. Liu, F. Shi, Y. Jiang and G. Liu, *Appl. Surf. Sci.*, **290**, 48 (2014); <https://doi.org/10.1016/j.apsusc.2013.10.185>
43. M. Mirak, M. Alizadeh, M. Ghaffari and M. Ashtiani, *J. Mech. Behav. Biomed. Mater.*, **62**, 282 (2016); <https://doi.org/10.1016/j.jmbbm.2016.05.016>
44. D. Pradhan, A. Wren, S. Misture and N. Mellott, *Mater. Sci. Eng. C*, **58**, 918 (2016); <https://doi.org/10.1016/j.msec.2015.09.059>
45. H. Fukuda and Y. Matsumoto, *Electrochim. Acta*, **50**, 5329 (2005); <https://doi.org/10.1016/j.electacta.2005.03.010>
46. Y. Ohko, S. Saitoh, T. Tatumasa and A. Fujishima, *J. Electrochem. Soc.*, **148**, B24 (2001); <https://doi.org/10.1149/1.1339030>
47. A. Majeed, J. He, L. Jiao, X. Zhong and Z. Sheng, *Nanoscale Res. Lett.*, **10**, 56 (2015); <https://doi.org/10.1186/s11671-015-0732-7>
48. L. Bait, L. Azzouz, N. Madaoui and N. Saoula, *Appl. Surf. Sci.*, **395**, 72 (2017); <https://doi.org/10.1016/j.apsusc.2016.07.101>
49. D.S.R. Krishna and Y. Sun, *Appl. Surf. Sci.*, **252**, 1107 (2005); <https://doi.org/10.1016/j.apsusc.2005.02.046>
50. G. Shen, Y. Chen, L. Lin, C. Lin and D. Scantlebury, *Electrochim. Acta*, **50**, 5083 (2005); <https://doi.org/10.1016/j.electacta.2005.04.048>
51. L. Bamoulid, M.-T. Maurette, D. De Caro, A. Guenbour, A. Ben Bachir, L. Aries, S. El Hajjaji, F. Benoît-Marqué and F. Ansart, *Surf. Coat. Technol.*, **202**, 5020 (2008); <https://doi.org/10.1016/j.surfcoat.2008.05.011>
52. C. Shan, X. Hou and K.L. Choy, *Surf. Coat. Technol.*, **202**, 2399 (2008); <https://doi.org/10.1016/j.surfcoat.2007.08.066>
53. T. Liu, F. Zhang, C. Xue, L. Li and Y. Yin, *Surf. Coat. Technol.*, **205**, 2335 (2010); <https://doi.org/10.1016/j.surfcoat.2010.09.028>
54. S. Berger, R. Hahn, P. Roy and P. Schmuki, *Phys. Status Solidi, B Basic Res.*, **247**, 2424 (2010); <https://doi.org/10.1002/pssb.201046373>
55. A.B. Neta, M.F. Mota, H.L. Lira, G.A. Neves and R.R. Menezes, *Ceramica*, **66**, 440 (2020); <https://doi.org/10.1590/0366-69132020663802905>
56. K. Indira, U.K. Mudali, T. Nishimura and N. Rajendran, *J. Bio. Tribo. Corros.*, **1**, 28 (2015); <https://doi.org/10.1007/s40735-015-0024-x>
57. Y. Alivov, M. Pandikunta, S. Nikishin and Z.Y. Fan, *Nanotechnology*, **20**, 225602 (2009); <https://doi.org/10.1088/0957-4484/20/22/225602>
58. J.E. Yoo and P. Schmuki, *J. Electrochem. Soc.*, **166**, C3389 (2019); <https://doi.org/10.1149/2.0381911jes>
59. M. Tak, H. Tomar and R.G. Mote, *Procedia CIRP*, **95**, 803 (2020); <https://doi.org/10.1016/j.procir.2020.01.140>
60. J. Harle, H. Kim, N. Mordan, J. Knowles and V. Salih, *Acta Biomater.*, **2**, 547 (2006); <https://doi.org/10.1016/j.actbio.2006.05.005>
61. A. Dehghanhadikolaei, J. Ansary and R. Ghoreishi, *Proc. Nat. Res. Soc.*, **2**, 02008 (2018).
62. X. Wang, F. Shi, X. Gao, C. Fan, W. Huang and X. Feng, *Thin Solid Films*, **548**, 34 (2013); <https://doi.org/10.1016/j.tsf.2013.08.056>
63. M. Advincula, F. Rahemtulla, R. Advincula, E. Ada, J. Lemons and S. Bellis, *Biomaterials*, **27**, 2201 (2006); <https://doi.org/10.1016/j.biomaterials.2005.11.014>
64. H. Paldan, S. Areva, T. Tirri, T. Peltola, T. Lindholm, L. Lassila, L. Pelliniemi, R.-P. Happonen and T.O. Närhi, *J. Mater. Sci. Mater. Med.*, **19**, 1283 (2008); <https://doi.org/10.1007/s10856-007-3234-z>
65. A. Ochsenbein, F. Chai, S. Winter, M. Traisnel, J. Breme and H. Hildebrand, *Acta Biomater.*, **4**, 1506 (2008); <https://doi.org/10.1016/j.actbio.2008.03.012>
66. S. Areva, H. Paldan, N.T. Peltola, M. Jokinen and M. Lindén, *J. Biomed. Mater. Res. A*, **70**, 169 (2004); <https://doi.org/10.1002/jbm.a.20120>
67. L. Guo, W. Feng and X. Liu, *Mater. Lett.*, **160**, 448 (2015); <https://doi.org/10.1016/j.matlet.2015.08.027>
68. G. Fu, P. Vary and C. Lin, *J. Phys. Chem. B*, **109**, 8889 (2005); <https://doi.org/10.1021/jp0502196>
69. A. Kubacka, M. Diez, D. Rojo, R. Bargiela, S. Ciordia, I. Zapico, J. Albar, C. Barbas, V.A.P. Martins Dos Santos, M. Fernandez-Garcia and M. Ferrer, *Sci. Rep.*, **4**, 4134 (2014); <https://doi.org/10.1038/srep04134>
70. A.E. Danks, S.R. Hall and Z. Schnepp, *Mater. Horiz.*, **3**, 91 (2016); <https://doi.org/10.1039/C5MH00260E>
71. M. Gardon and J.M. Guilemany, *J. Therm. Spray Technol.*, **23**, 577 (2014); <https://doi.org/10.1007/s11666-014-0066-5>
72. A. Dehghanhadikolaei and B. Fotovvati, *Materials*, **12**, 1795 (2019); <https://doi.org/10.3390/ma12111795>
73. A. Jemat, M.J. Ghazali, M. Razali, Y. Otsuka and A. Rajabi, *Ceram. Int.*, **44**, 4271 (2018); <https://doi.org/10.1016/j.ceramint.2017.12.008>
74. R.S. Pillai, M. Frasnelli and V.M. Sglavo, *Ceram. Int.*, **44**, 1328 (2018); <https://doi.org/10.1016/j.ceramint.2017.08.113>
75. R. Narayanan, S.K. Seshadri, T.Y. Kwon and K.H. Kim, *J. Biomed. Mater. Res. B Appl. Biomater.*, **85**, 279 (2008); <https://doi.org/10.1002/jbm.b.30932>
76. K. Ahmed and M. Shoeib, *Sch. J. Appl. Sci. Res.*, **1**, 20 (2018).
77. H. Gutzmann, S. Freese, F. Gartner and T. Klassen, *J. Therm. Spray Technol.*, **20**, 292 (2011); <https://doi.org/10.1007/s11666-010-9563-3>
78. N.I. Omar, S. Selvami, M. Kaisho, M. Yamada, T. Yasui and M. Fukumoto, *Coatings*, **10**, 991 (2020); <https://doi.org/10.3390/coatings10100991>

79. P. Poza and M.A. Garrido-Maneiro, *Prog. Mater. Sci.*, **123**, 100839 (2022); <https://doi.org/10.1016/j.pmatsci.2021.100839>
80. S. Pathak and G.C. Saha, *Coatings*, **7**, 122 (2017); <https://doi.org/10.3390/coatings7080122>
81. M. Winnicki, A. Baszczuk, M. Jasiorski, B. Borak and A. Malachowska, *Surf. Coat. Technol.*, **371**, 194 (2019); <https://doi.org/10.1016/j.surfcoat.2018.09.057>
82. K. Schmidt, S. Buhl, N. Davoudi, C. Godard, R. Merz, I. Raid, E. Kerschler, M. Kopnarski, C. Müller-Renno, S. Ripperger, J. Seewig, C. Ziegler and S. Antonyuk, *Surf. Coat. Technol.*, **309**, 749 (2017); <https://doi.org/10.1016/j.surfcoat.2016.10.091>
83. J.O. Kliemann, H. Gutzmann, F. Gärtner, H. Hübner, C. Borchers and T. Klassen, *J. Therm. Spray Technol.*, **20**, 292 (2011); <https://doi.org/10.1007/s11666-010-9563-3>
84. H. Hajipour, A. Abdollah-Zadeh, H. Assadi, E. Taheri-Nassaj and H. Jahed, *J. Therm. Spray Technol.*, **27**, 1542 (2018); <https://doi.org/10.1007/s11666-018-0782-3>
85. T. Hussain, *Key Eng. Mater.*, **533**, 53 (2013); <https://doi.org/10.4028/www.scientific.net/KEM.533.53>
86. S. Kamnis and S. Gu, *Chem. Eng. Sci.*, **61**, 5427 (2006); <https://doi.org/10.1016/j.ces.2006.04.005>
87. J.A. Hearley and J.A. Little, *Surf. Coat. Technol.*, **33**, 671 (2000).
88. M. Li and P.D. Christofides, *Chem. Eng. Sci.*, **58**, 849 (2003); [https://doi.org/10.1016/S0009-2509\(02\)00616-4](https://doi.org/10.1016/S0009-2509(02)00616-4)
89. G.J. Yang, C.J. Li, F. Han and A. Ohmori, *Thin Solid Films*, **466**, 81 (2004); <https://doi.org/10.1016/j.tsf.2004.02.015>
90. M. Bozorgtabar and M. Jafarpour, *Am. J. Eng. Res.*, **4**, 82 (2015).
91. C. -J. Li, G.-J. Yang, Y.-Y. Wang, C.-X. Li, F.-X. Ye and A. Ohmori, *Mater. Trans.*, **47**, 1690 (2006); <https://doi.org/10.2320/matertrans.47.1690>
92. M. Bozorgtabar, M. Rahimpour and M. Salehi, *Mater. Lett.*, **64**, 1173 (2010); <https://doi.org/10.1016/j.matlet.2010.02.042>
93. M. Li and P.D. Christofides, *J. Therm. Spray Technol.*, **18**, 753 (2009); <https://doi.org/10.1007/s11666-009-9309-2>
94. N. Stiegler, D. Bellucci, G. Bolelli, V. Cannillo, R. Gadow, A. Killinger, L. Lusvarghi and A. Sola, *J. Therm. Spray Technol.*, **21**, 275 (2012); <https://doi.org/10.1007/s11666-011-9724-z>
95. H. Li, K. Khor and P. Cheang, *Biomaterials*, **23**, 85 (2002); [https://doi.org/10.1016/S0142-9612\(01\)00082-5](https://doi.org/10.1016/S0142-9612(01)00082-5)
96. G. Bolelli, R. Giovanardi, L. Lusvarghi and T. Manfredini, *Corros. Sci.*, **48**, 3375 (2006); <https://doi.org/10.1016/j.corsci.2006.03.001>
97. Z.G. Ban and L.L. Shaw, *J. Spray Technol.*, **12**, 112 (2003); <https://doi.org/10.1361/105996303770348564>
98. L. Visai, L. De Nardo, C. Punta, L. Melone, A. Cigada, M. Imbriani and C.R. Arciola, *Int. J. Artif. Organs*, **34**, 929 (2011); <https://doi.org/10.5301/ijao.5000050>
99. B. Song, Z. Pala, K. Voisey and T. Hussain, *Surf. Coat. Technol.*, **318**, 224 (2017); <https://doi.org/10.1016/j.surfcoat.2016.07.046>
100. R.B. Heimann and H.D. Lehmann, *Bioceramic Coatings for Medical Implants: Trends and Techniques*, Wiley, Chap. 6, pp 253-294 (2015).
101. G. Bolelli, R. Cannillo, R. Gadow, A. Killinger, L. Lusvarghi and J. Rauch, *Surf. Coat. Technol.*, **203**, 1722 (2009); <https://doi.org/10.1016/j.surfcoat.2009.01.006>
102. R. Gadow, A. Killinger and J. Rauch, *J. Therm. Spray Technol.*, **17**, 655 (2008); <https://doi.org/10.1007/s11666-008-9264-3>
103. U. Brohede, J. Forsgren, S. Roos, A. Mhranyan, H. Engqvist and M. Strömme, *J. Mater. Sci. Mater. Med.*, **20**, 1859 (2009); <https://doi.org/10.1007/s10856-009-3749-6>
104. B.M. Kang, W.J. Jeong, G.C. Park, D.J. Yoon, H.G. Ahn and Y.S. Lim, *J. Nanosci. Nanotechnol.*, **15**, 6020 (2015); <https://doi.org/10.1166/jnn.2015.10417>
105. J.M. Lackner, W. Waldhauser, R. Ebner, B. Major and T. Schoberl, *Surf. Coat. Technol.*, **180-181**, 585 (2004); <https://doi.org/10.1016/j.surfcoat.2003.10.099>
106. S. Murugesan, P. Kuppusami, N. Parvathavarthini and E. Mohandas, *Surf. Coat. Technol.*, **201**, 7713 (2007); <https://doi.org/10.1016/j.surfcoat.2007.03.004>
107. M. Filipescu, A. Palla-Papavlu and D. Maria, *Functional Metal Oxide Thin Films Grown by Pulsed Laser Deposition, Crystalline and Non-crystalline Solids*, IntechOpen (2016); <https://doi.org/10.5772/62986>
108. E. Bogdanov, Y. Vavllina, N. Shusharina, A. Goykhman and M. Patrushev, *J. Nanomed. Nanotechnol.*, **5**, 1 (2014); <https://doi.org/10.4172/2157-7439.1000189>
109. M.K. Ji, S.W. Park, K. Lee, I.C. Kang, K.D. Yun, H.S. Kim and H.P. Lim, *J. Adv. Prosthodont.*, **7**, 166 (2015); <https://doi.org/10.4047/jap.2015.7.2.166>
110. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, A.A. Grigorieva IV and A.A. Firsov, *Science*, **306**, 666 (2004); <https://doi.org/10.1126/science.1102896>
111. N. Ohtsu, K. Saito, K. Asami and T. Hanawa, *Surf. Coat. Technol.*, **200**, 5455 (2006); <https://doi.org/10.1016/j.surfcoat.2005.07.003>
112. M. Hamdi and A. Ide-Ektessabi, *Surf. Coat. Technol.*, **163-164**, 362 (2003); [https://doi.org/10.1016/S0257-8972\(02\)00625-4](https://doi.org/10.1016/S0257-8972(02)00625-4)
113. Z.S. Luo, F.Z. Cui, Q.L. Feng, H.D. Li, X.D. Zhu and M. Spector, *Surf. Coat. Technol.*, **131**, 192 (2000); [https://doi.org/10.1016/S0257-8972\(00\)00824-0](https://doi.org/10.1016/S0257-8972(00)00824-0)
114. S. Boukrouh, R. Bensaha, S. Bourgeois, E. Finot and M.C. Marco de Lucas, *Thin Solid Films*, **516**, 6353 (2008); <https://doi.org/10.1016/j.tsf.2007.12.150>
115. S. Davidsdóttir, R. Shabadi, A.C. Galca, I.H. Andersen, K. Dirscherl and R. Ambat, *Appl. Surf. Sci.*, **313**, 677 (2014); <https://doi.org/10.1016/j.apsusc.2014.06.047>
116. C.J. Tavares, J. Vieira, L. Rebouta, G. Hungerford, P. Coutinho, V. Teixeira, J.O. Carneiro and A.J. Fernandes, *Mater. Sci. Eng. B-Solid State Mater. Adv. Technol.*, **138**, 139 (2007); <https://doi.org/10.1016/j.mseb.2005.11.043>
117. W. Schönberger, H. Bartzsch, S. Schippel and T. Bachmann, *Surf. Coat. Technol.*, **293**, 16 (2016); <https://doi.org/10.1016/j.surfcoat.2015.12.073>
118. X. Wang, F. Prokert, H. Reuther, M.F. Maitz and F. Zhang, *Surf. Coat. Technol.*, **185**, 12 (2004); <https://doi.org/10.1016/j.surfcoat.2003.12.002>
119. W. Schönberger, H. Bartzsch, S. Schippel and T. Bachmann, *Surf. Coat. Technol.*, **293**, 16 (2016); <https://doi.org/10.1016/j.surfcoat.2015.12.073>
120. A.Y. Goikman, S.A. Sheludyakov and E.A. Bogdanov, *J. Novel Mater.: Coats Nanoeng.*, **674**, 195 (2011); <https://doi.org/10.4028/www.scientific.net/MSF.674.195>
121. J. Xu, Y. Li, X. Zhou, Y. Li, Z.D. Gao, Y.Y. Song and P. Schmuki, *Chem. Eur. J.*, **22**, 3947 (2016); <https://doi.org/10.1002/chem.201505173>
122. S. Reghunath, D. Pinheiro and K.R. Sunaja Devi, *App. Surf. Sci. Adv.*, **3**, 100063 (2021); <https://doi.org/10.1016/j.apsadv.2021.100063>
123. L. Besra and M. Liu, *Progr. Mater. Sci.*, **52**, 1 (2007); <https://doi.org/10.1016/j.pmatsci.2006.07.001>
124. I. Gibson and W. Bonfield, *J. Mater. Sci. Mater. Med.*, **13**, 685 (2002); <https://doi.org/10.1023/A:1015793927364>
125. H. Shalom, Y. Feldman, R. Rosentsveig, I. Pinkas, I. Kaplan-Ashiri, A. Moshkovich, V. Perfilyev, L. Rapoport and R. Tenne, *Int. J. Mol. Sci.*, **19**, 657 (2018); <https://doi.org/10.3390/ijms19030657>
126. D.H. He, P. Wang, P. Liu, X.K. Liu, F.C. Ma and J. Zhao, *Surf. Coat. Technol.*, **301**, 6 (2016); <https://doi.org/10.1016/j.surfcoat.2016.07.005>
127. L. Yan, Y. Xiang, J. Yu, Y. Wang and W. Cui, *ACS Appl. Mater. Interfaces*, **9**, 5023 (2017); <https://doi.org/10.1021/acsami.6b15979>
128. B. Bakin, T. Koc Delice, U. Tiric, I. Birlik and F. Ak Azem, *Surf. Coat. Technol.*, **301**, 29 (2016); <https://doi.org/10.1016/j.surfcoat.2015.12.078>

129. R. Chakraborty, V.S. Seesala, S. Sengupta, S. Dhara, P. Saha, K. Das and S. Das, *Surf. Interfaces*, **10**, 1 (2018);
<https://doi.org/10.1016/j.surfint.2017.11.002>
130. X. Zhao, T. Hu, H. Li, M. Chen, S. Cao, L. Zhang and X. Hou, *Appl. Surf. Sci.*, **257**, 3612 (2011);
<https://doi.org/10.1016/j.apsusc.2010.11.088>
131. A. Tahmasbi Rad, M. Solati-Hashjin, N.A.A. Osman and S. Faghihi, *Ceram. Int.*, **40**, 12681 (2014);
<https://doi.org/10.1016/j.ceramint.2014.04.116>
132. M. Sankar, S. Suwas, S. Balasubramanian and G. Manivasagam, *Surf. Coat. Technol.*, **309**, 840 (2017);
<https://doi.org/10.1016/j.surfcoat.2016.10.077>
133. T. Kokubo, H. Kushitani, S. Sakka, T. Kitsugi and T. Yamamuro, *J. Biomed. Mater. Res.*, **24**, 721 (1990);
<https://doi.org/10.1002/jbm.820240607>
134. A.L. Escada, J.P.B. Machado, S.G. Schneider, M.C.R.A. Rezende and A.P.R.A. Claro, *J. Mater. Sci. Mater. Electron.*, **22**, 2457 (2011);
<https://doi.org/10.1007/s10856-011-4434-0>
135. W. Xia, C. Lindahl, J. Lausmaa, P. Borchardt, A. Ballo, P. Thomsen and H. Engqvist, *Acta Biomater.*, **6**, 1591 (2010);
<https://doi.org/10.1016/j.actbio.2009.10.030>
136. B. Burnat, J. Robak, A. Leniart, I. Piwoński and D. Batory, *Ceram. Int.*, **43**, 13735 (2017);
<https://doi.org/10.1016/j.ceramint.2017.07.086>
137. B. Burnat, J. Robak, D. Batory, A. Leniart, I. Piwoński, S. Skrzypek and M. Brycht, *Surf. Coat. Technol.*, **280**, 291 (2015);
<https://doi.org/10.1016/j.surfcoat.2015.09.018>
138. J. Coreño, A. Martínez, O.A. Coreño, A. Bolarín and F. Sánchez, *J. Biomed. Mater. Res. A*, **64**, 131 (2003);
<https://doi.org/10.1002/jbm.a.10395>
139. M. Uchida, H.M. Kim, T. Kokubo, S. Fujibayashi and T. Nakamura, *J. Biomed. Mater. Res. A*, **64**, 164 (2003);
<https://doi.org/10.1002/jbm.a.10414>
140. T. Peltola, M. Jokinen, H. Rahiala, J.I. Heikkilä, I. Kangasniemi, M. Pääsi and A. Yli-Urpo, *J. Biomed. Mater. Res.*, **51**, 200 (2000);
[https://doi.org/10.1002/\(SICI\)1097-4636\(200008\)51:2<200::AID-JBM8>3.0.CO;2-Z](https://doi.org/10.1002/(SICI)1097-4636(200008)51:2<200::AID-JBM8>3.0.CO;2-Z)
141. P. Li, C. Ohtsuki, T. Kokubo, K. Nakanishi, N. Soga and K. deGroot, *J. Biomed. Mater. Res.*, **28**, 7 (1994);
<https://doi.org/10.1002/jbm.820280103>