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Enhanced Antibacterial Performance of Functionally Graded Biomaterial Coatings on Ti-6Al-4V Alloy

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Abstract

The electrophoretic deposition (EPD) technique was used to prepare seven-layered functionally graded hydroxyapatite/titanium dioxide (HAp/TiO_2) coatings on Ti–6Al–4V alloy for biomedical implant applications. The coating structure was designed with a compositional gradient from pure TiO_2 near the substrate to pure HAp on the outer surface, so as to combine the corrosion resistance of TiO_2 with the bioactivity of HAp. The coated samples were heat-treated at 950°C for one hour under an argon atmosphere to improve the coating stability and phase formation after deposition.

The structural characteristics of the coatings were evaluated by X-ray diffraction (XRD). The obtained results confirmed the presence of hydroxyapatite as well as anatase and rutile phases of titanium dioxide. Furthermore, other calcium phosphate phases were observed due to the partial decomposition of hydroxyapatite during the sintering process. The corrosion behavior was evaluated by potentiodynamic polarization tests in Ringer's solution, where the coated samples showed better corrosion resistance than the uncoated Ti–6Al–4V alloy. with corrosion characteristics gradually increasing from S1 to S7. S7 coating showed the highest noble corrosion potential (Ecorr = −0.23 V), lowest corrosion current density (Icorr = 2.02 μA/cm2) and lowest corrosion rate (CR = 0.018 mpy). The antibacterial activity against *Escherichia coli* was also evaluated by the inhibition zone method. The produced coatings showed good antibacterial activity and reduced the development of E. coli bacteria. The results indicate that functionally graded HAp/TiO2 coatings can greatly improve the surface properties of Ti-6Al-4V alloy concurrently boosting corrosion resistance and antibacterial performance and have great potential in biomedical implant applications.

Keywords: TiO_2, Functionally graded coatings, Ti-6Al-4V alloy, HAp, Antibacterial activity, Corrosion resistance.

Introduction

Titanium and its alloys are widely employed in implant fabrication for load-bearing applications because of their excellent biocompatibility and mechanical qualities. However, they have low osteoconductivity, and several surface modifications have been proposed to improve their biological characteristics [1]. Biomaterials have become increasingly significant in modern medicine due to their increased use in orthopedic and dental implants. Ti–6Al–4V alloy is used extensively in biomedical applications because of its advantageous strength to weight ratio and long-term performance in physiologic environments [2],[3]. Titanium alloys, however, are not without their disadvantages. Prolonged contact with physiological fluids may cause gradual release of ions and local corrosion, which may negatively affect the surrounding tissues [4]. In addition, bacterial adhesion and biofilm formation on the implant surface are major concerns that could lead to implant-related infections and eventual failure of the implant [5]. Considerable efforts have therefore been made to improve the surface properties of titanium implants while retaining the favourable bulk properties.

Surface coating technology is an effective method to improve the biological and electrochemical performances of metallic implants. Among the different coating materials, hydroxyapatite (HAp) has attracted considerable interest due to its similarity to the mineral component of natural bone [6]. Hydroxyapatite coatings promote osseointegration, improve bone-implant bonding and enhance the biological response of implanted devices. Furthermore, HAp is highly biocompatible and bioactive, and is one of the most widely investigated ceramic biomaterials for orthopedic and dental applications [7]. Another possible coating material is titanium dioxide (TiO2) due to its excellent chemical stability, corrosion resistance and good affinity with biological tissues. The presence of TiO2 on the surface of implants can increase surface passivation and add further protection against the corrosive physiological environment. Moreover, previous studies have demonstrated that TiO2 -based coatings may contribute to a decrease in bacterial adhesion and an improvement in the long-term durability of biomedical implants.

Functionally graded coatings (FGCs) have been developed recently as an advanced strategy to overcome the limitations of conventional single-layer coatings. Functionally graded structures provide a gradual variation in composition and properties through the coating thickness, resulting in improved adhesion strength, reduced residual stresses and improved mechanical reliability. Such coatings are especially attractive for biomedical applications as they combine the desirable properties of multiple materials in a single coating system [8]. Electrophoretic deposition (EPD) is one of the existing coating fabrication methods that has gained considerable interest due to its simplicity, low cost, and ability to produce homogeneous coatings with controlled thickness and composition. Besides, EPD allows the fabrication of multilayer and functionally graded coatings with complex architectures, making it highly suitable for biomedical surface engineering applications [9]. Recent studies have shown that electrophoretic deposition is effective in fabricating functionally graded HAp/TiO2 coatings with enhanced corrosion resistance and biological performance. Compared with conventional monolayer coatings, graded structures provide smoother compositional transitions, reduced residual stresses and improved adhesion strength. In addition, TiO2-containing coatings have shown antibacterial effects through inhibition of bacterial adhesion and alteration of bacterial membrane integrity [10].

Therefore, the present work aims to fabricate seven-layered functionally graded hydroxyapatite/titanium dioxide (HAp/TiO2) coatings on Ti–6Al–4V alloy by electrophoretic deposition technique. The prepared coatings were characterized by X-ray diffraction analysis and their corrosion resistance and antibacterial behavior were evaluated to assess their potential use in biomedical implant applications.

2.Materials and Method

2.1 Materials

The materials used in this study were Ti-6Al-4V alloy substrate, HAp powder, TiO2 powder, PEI and 100% ethanol. Ti-6Al-4V alloy was selected as the substrate material because it is widely used in bone and dental implants. HAP was selected as a bioactive material with excellent stimulating properties of bone growth. TiO2 was used to increase corrosion resistance and antibacterial properties and PEI was used as a charging and dispersing agent. Absolute ethanol was used as a solvent in the electrolytic deposition process. All compounds were used as received without further processing.

2.2 Surface Preparation of Ti-6Al-4V Substrates

Prior to the coating deposition process, Ti-6Al-4V substrate was polished with SiC sandpaper of grit 180-3000. To remove impurities and oxides from the substrate surface, the samples were washed with distilled water and exposed to ultraviolet light, followed by acetone. Finally, the samples were dried and placed in a silica gel-based desiccant before being used for microstructural and electrochemical analyses. UV treatment was mainly used for surface sterilization before deposition of the coating. The samples were then cleaned using acetone and dried before usage.

2.3 Preparation of Coating Suspensions

The fabrication of a graded coating consisted of seven successive stages of deposition, each stage being about 8.5 s long, for a total deposition time of 60 s. The graded coating was fabricated by sequential deposition of suspensions S1–S7 as shown in Table 1. In the first stage, a pure titanium dioxide (TiO_2) layer was deposited directly onto the Ti-6Al-4V substrate using suspension S1. Five intermediate composite layers of TiO_2/HAp with different compositions were sequentially deposited using suspensions S2, S3, S4, S5 and S6, followed by a pure hydroxyapatite (HAp) outer layer applied by suspension S7. The HAp content increased progressively from 0% at the substrate-coating interface to 100% at the outermost surface, resulting in a smooth and continuous compositional gradient throughout the coating thickness.

Table 1. Composition of Functionally Graded Coating Suspensions

Solution No.	Layer	TiO_2 (g)	Hap (g)	Ethanol (ml)	PEI (g/L)
S1	1st	10	0	200	6
S2	2nd	8	2	200	6
S3	3rd	6	4	200	6
S4	4th	5	5	200	6
S5	5th	4	6	200	6
S6	6th	2	8	200	6
S7	7th	0	10	200	6

Seven deposition layers were used to obtain a progressive compositional shift between TiO_2 and HAp. This design decreases the interfacial stress concentration, increases the coating adherence and lessens the risk of fracture development during heat treatment.

2.4 Electrophoretic Deposition of Functionally Graded Coatings

The electrophoretic deposition was carried out with a DC power supply where 316L stainless steel was used as the anode and Ti–6Al–4V alloy was used as the cathode. The electrodes were fixed in the suspension at a distance of 15 mm. The films were deposited at a voltage of 20 V, a deposition time of 60 s and an inter-electrode distance of 15 mm were selected based on prior published studies and preliminary experimental observations. The parameters gave stable deposition conditions, allowed uniform coatings to be formed and minimized the occurrence of coating defects such as cracking and delamination. Therefore, they were utilized for the development of the functionally graded HAp/TiO2 coatings.

2.5 Fabrication of the functionally Graded Structure

The gradient coating structure was fabricated through seven successive deposition steps. The first coating layer was pure TiO2 deposited directly on the substrate, followed by five intermediate layers with varying HAp/TiO2 ratios. The outermost layer of the coating was pure HAp. The aim of this compositional gradient was to decrease the interfacial tension and enhance the coating adhesion.

2.6 Heat treatment

All samples were dried for 24 hours in the air at ambient temperature and then ultimately heat-treated in an argon furnace at 950 C ° for one hour.

The sintering temperature was chosen at 950°C to optimize the coating densification and phase development without affecting the substrate integrity. Corresponding temperatures have been successfully used in prior experiments with HAp/TiO coatings.

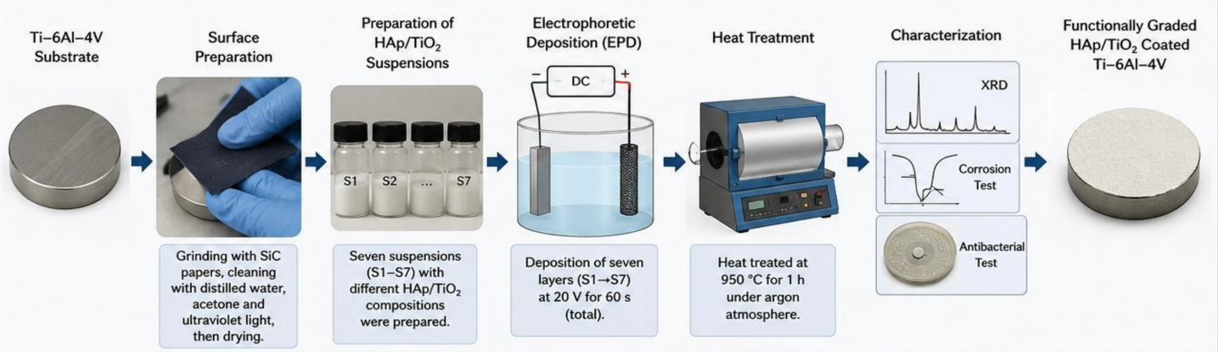

Figure1. Flow chart of the experimental procedure used in the present study.

2.7 Characterisation of the coatings

2.7.1 XRD Analysis

X-ray diffraction (XRD) is an effective analytical method for determining the molecular structure of crystalline materials by measuring the diffraction of X-rays through a sample. The resulting interference patterns can be used to infer the lattice structure and thus allow analysis of factors such as unit cell size, crystal symmetry, strain and defects [11].

The crystalline phases in the coated samples after heat treatment were determined by XRD analysis using a Philips PW 1480 X-ray diffraction spectrometer.

The presence of hydroxyapatite, anatase and rutile phases confirms the successful fabrication of the functionally graded coating. The presence of minor calcium phosphate phases is associated with partial thermal decomposition of hydroxyapatite during sintering, which has been reported previously for HAp-based coatings treated at elevated temperatures.

2.7.2 Corrosion and Antibacterial Evaluation

A dynamic polarization test by potentiometer (EG&G 263 A) was used to determine the corrosion resistance of untreated and coated samples [12]. Samples were submerged in Ringer’s electrolyte solution, which simulates bodily fluids. A saturated silver/silver chloride electrode was used as the reference electrode, and a platinum electrode was used as the counter electrode. Samples were utilized as working electrodes. The Ringer’s solution was prepared at pH 5 and 37 ± 2 0C. All the electrochemical tests were performed at 37±2 °C for all the samples.

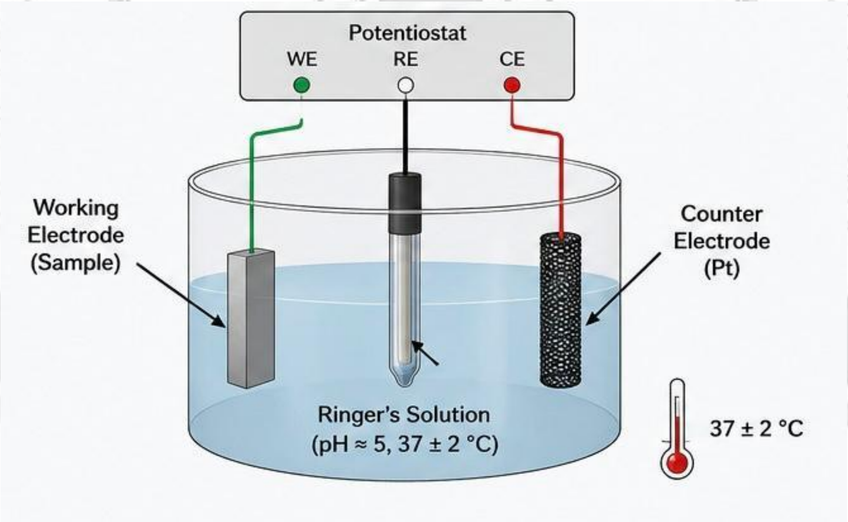

Figure 2. Schematic illustration of the electrochemical corrosion testing setup.

In this investigation, the Gram-negative Escherichia coli (E. coli, ATCC8739) was employed as a model of bacteria producing degradation in order to evaluate the antibacterial capabilities of the produced surfaces. The antibacterial activity was determined using the zone of inhibition technique. One million bacterial cells of a single strain were distributed on an agar plate with a sterile brush and the plate was incubated in the presence of the solution. The free zone of growth surrounding the sample reflects the sensitivity of the bacteria to the solution and the inhibition zone will be observed on the agar plate.

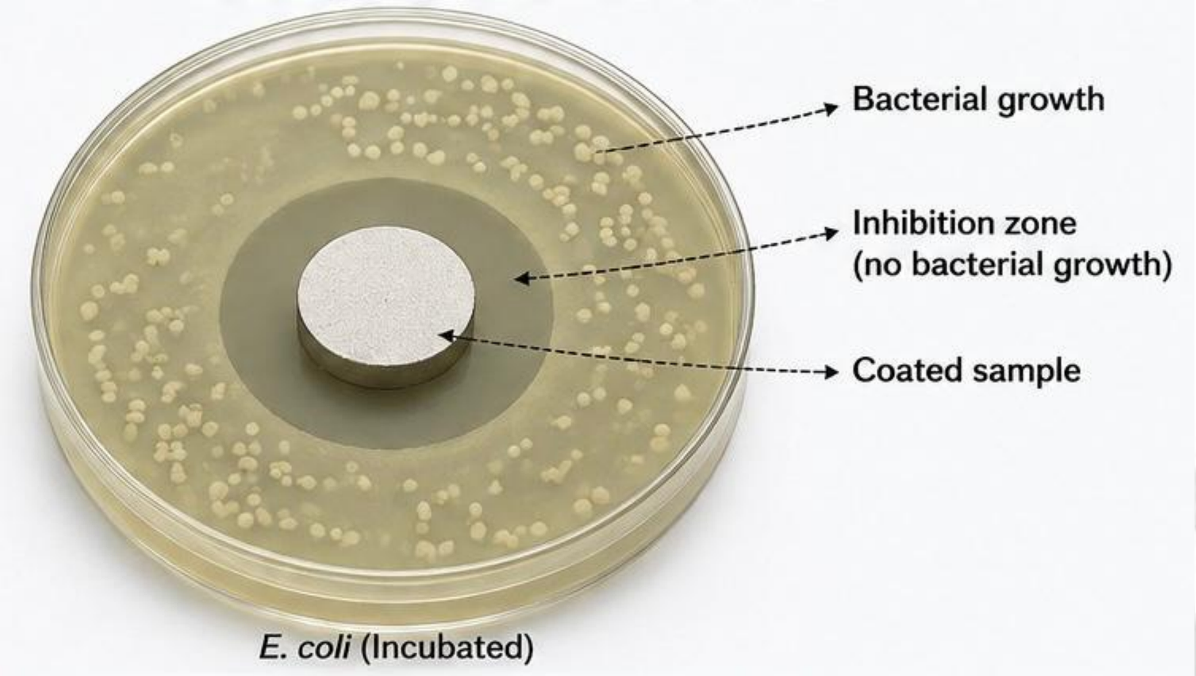

Figure 3. Schematic representation of the inhibition zone method used for antibacterial evaluation.

3. Results of Tests and Discussion

3.1. Results of X-Ray Diffraction Test

The X-Ray Diffraction patterns of the seven-layer functionally graded HAp/TiO_2 coatings sintered at 950°C for 1 h under an argon atmosphere are shown in Figure 4. The results showed the existence of HAp along with anatase and rutile phases of TiO2, indicating successful formation of the graded coating. The heat treatment promoted partial anatase-to-rutile transformation and the major crystalline phases were stable after sintering. Minor peaks related to calcium phosphate phases were also observed, indicating partial phase evolution during the thermal process.

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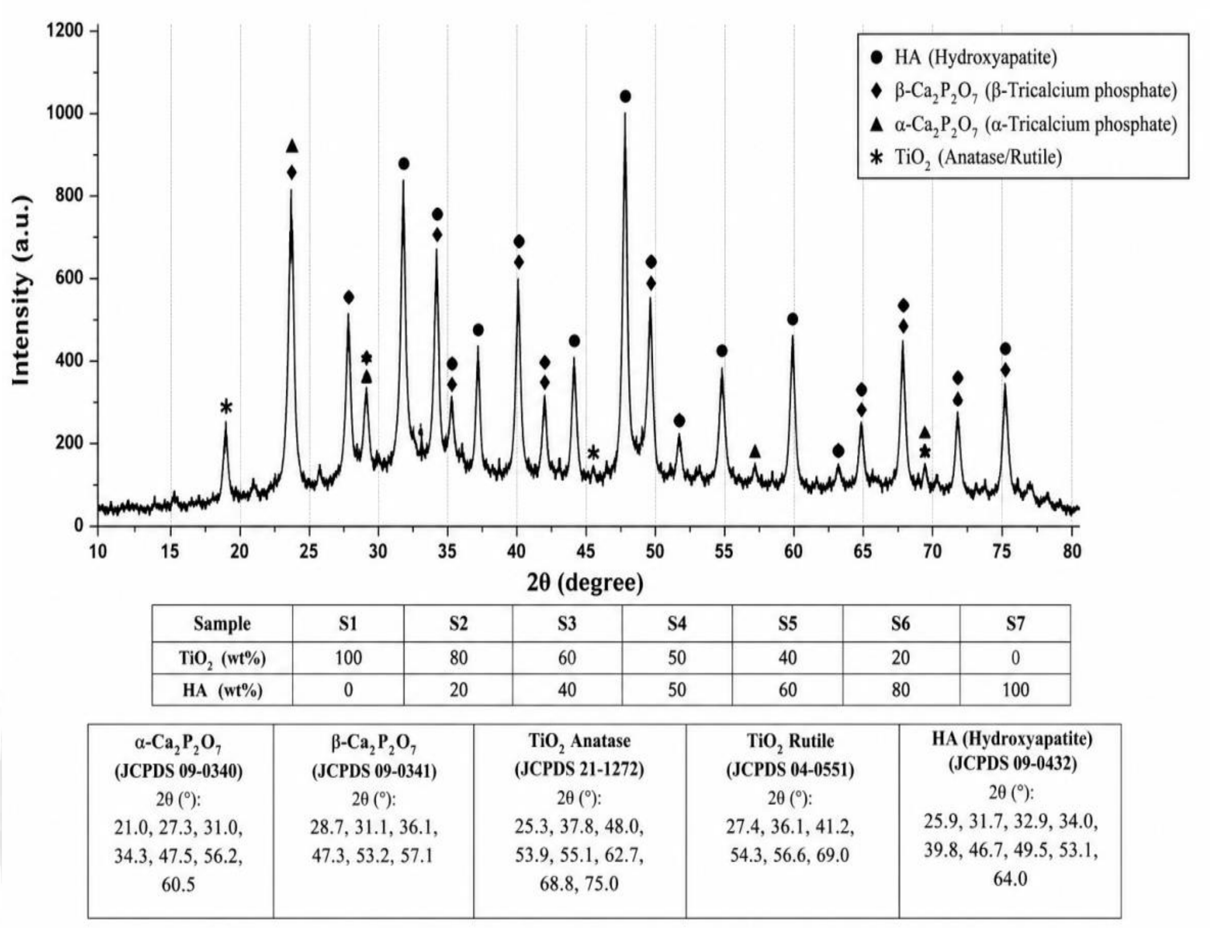

Sample	S1	S2	S3	S4	S5	S6	S7
TiO_2 (wt%)	100	80	60	50	40	20	0
HA (wt%)	0	20	40	50	60	80	100

α-$Ca_2P_2O_7$ (JCPDS 09-0340)	β-$Ca_2P_2O_7$ (JCPDS 09-0341)	TiO_2 Anatase (JCPDS 21-1272)	TiO_2 Rutile (JCPDS 04-0551)	HA (Hydroxyapatite) (JCPDS 09-0432)
2θ (°): 21.0, 27.3, 31.0, 34.3, 47.5, 56.2, 60.5	2θ (°): 28.7, 31.1, 36.1, 47.3, 53.2, 57.1	2θ (°): 25.3, 37.8, 48.0, 53.9, 55.1, 62.7, 68.8, 75.0	2θ (°): 27.4, 36.1, 41.2, 54.3, 56.6, 69.0	2θ (°): 25.9, 31.7, 32.9, 34.0, 39.8, 46.7, 49.5, 53.1, 64.0

Figure 4. X-ray diffraction pattern of the functionally graded HAp/TiO2 coated specimen

In addition to HAp and TiO2 phases, a few small diffraction peaks were also observed, which might be attributed to α-Ca2P2O7 and β-Ca2P2O7 phases. These phases are formed by partial decomposition of hydroxyapatite during the temperature sintering process. The formation of these calcium phosphate phases suggests that phase evolution occurred in the coating, while the overall bioactive nature of the deposited layer was maintained.

Similar results were reported by Fathi et al. (2008), who confirmed the coexistence of HAp and TiO_2 phases after thermal treatment [13].

The presence of hydroxyapatite, anatase and rutile phases confirms the successful fabrication of the functionally graded coating. The coexistence of these phases is beneficial because hydroxyapatite enhances bioactivity, while titanium dioxide contributes to corrosion resistance and surface stability. In addition, minor calcium phosphate phases were detected, which may be attributed to the partial thermal decomposition of hydroxyapatite during sintering at elevated temperatures. Similar phase transformations have been reported previously for HAp-based coatings subjected to heat treatment.

3.2 Electrochemical Corrosion

Figure 5 illustrates the potentiodynamic polarization curves of the uncoated Ti6Al4V alloy together with HAp, TiO_2, and functionally graded coating (FGC) samples immersed in simulated body fluid (Ringer's solution). Polarization curves are commonly employed to evaluate the electrochemical corrosion behavior of metallic materials. In general, increased corrosion resistance can be interpreted as increased probability of free corrosion and lower current passivation yield was obtained.

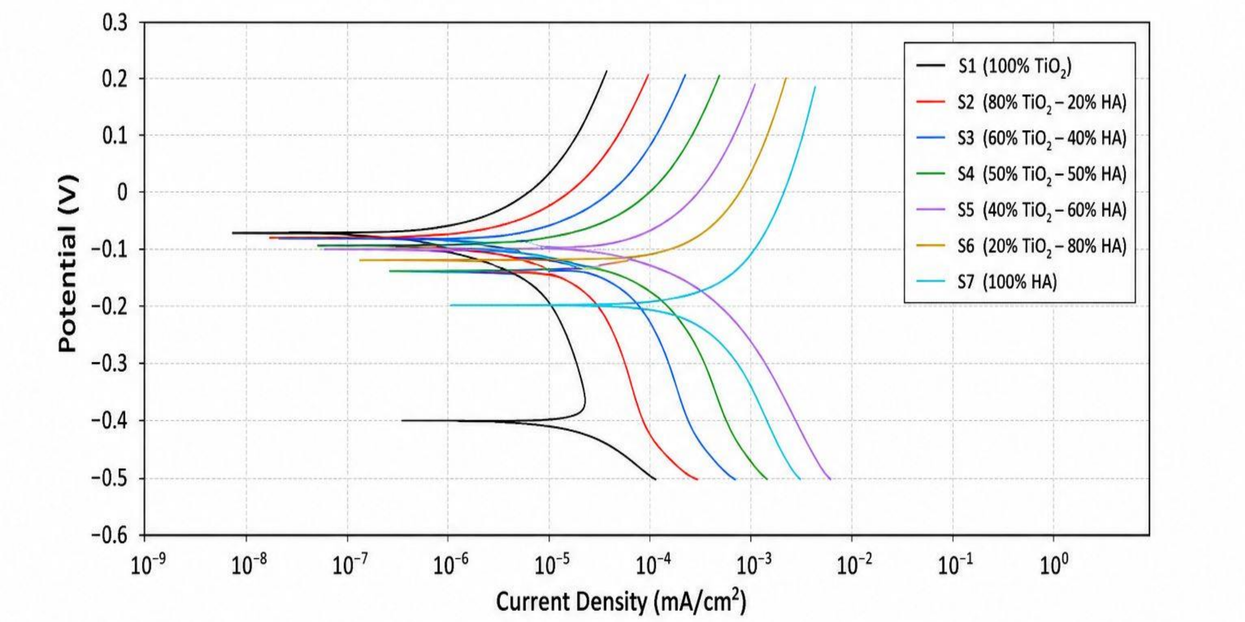

Figure 5. Potentiodynamic polarisation curves for coated and uncoated samples in Ringer's solution

Table2. Electrochemical corrosion parameters (Ecorr and Icorr) from potentiodynamic polarization experiments in Ringer's solution.

Media	Sample	E_{corr} (V)	I_{corr} ($\mu A/cm^2$)	CR (mpy)	$R_P * (10^{-3})(\Omega.cm^2)$
Ringers Solution	S1 (100% TiO_2)	-0.84	20.09	0.176	1.29
	S2 (80% TiO_2 - 20% HA)	-0.58	9.75	0.085	2.65
	S3 (60% TiO_2 - 40% HA)	-0.46	6.21	0.054	4.16
	S4 (50% TiO_2 – 50% HA)	-0.36	4.12	0.036	6.27
	S5 (40% TiO_2 - 60% HA)	-0.31	3.21	0.028	8.03
	S6 (20% TiO_2 - 80% HA)	-0.27	2.68	0.023	9.34
	S7 (100% HA)	-0.23	2.02	0.018	11.85

The obtained corrosion behavior agrees with the findings of Hamil et al. (2020), who observed a significant improvement in corrosion resistance after coating Ti–6Al–4V alloy with TiO_2 [14].

3.3 Anti-bacterial Study

The prepared functionally graded HAp/TiO 2 coatings were tested for their antibacterial activity against Escherichia coli by the inhibition zone method . The antibacterial response of the coated specimens after incubation is given in Figure 6 . The coated samples exhibited clear inhibition zones around the specimens indicating their ability to suppress bacterial growth. The antibacterial activity was found to be composition dependent, in such a manner that samples with higher content of TiO 2 presented more pronounced antibacterial behavior. This effect can be attributed to the ability of TiO 2 -containing surfaces to reduce bacterial adhesion and affect the integrity of the bacterial cell membrane . Since the antibacterial tests were done under normal laboratory conditions without UV irradiation, the generation of photocatalytic reactive oxygen species was not considered as the main antibacterial mechanism. On the contrary, the HAp-rich layers helped to increase the biocompatibility of the coating, while keeping the antibacterial performance. Overall, the functionally graded coating showed better biological performance than the uncoated Ti–6Al–4V substrate, suggesting its potential biomedical implant applications where the prevention of bacterial colonization is very important. Balaei et al. (2024) also demonstrated similar activity of TiO2 containing coatings that inhibited the bacterial growth and improved the surface functionality [15].

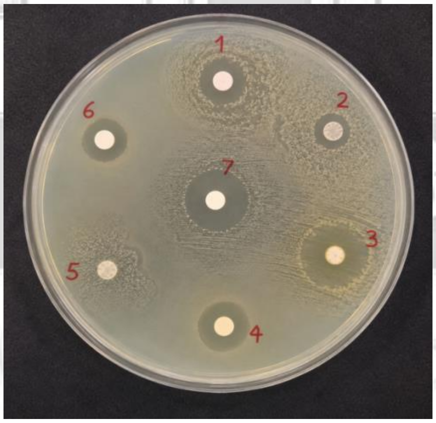

Figure 6: Images of the anti-bacterial tests of HAp/TiO2 against E. coli.

4. Conclusions

The XRD study confirmed that the expected crystalline phases formed after sintering at 950 °C were hydroxyapatite (HAp) and titanium dioxide in anatase and rutile form. The partial disintegration of hydroxyapatite following heat treatment also resulted in the identification of minor calcium phosphate phases. The introduction of polyethyleneimine (PEI) into the HAp/TiO2 solution facilitated the stability of the electrophoretic deposition bath resulting in the production of homogeneous coatings. Also, the functionally graded HAp/TiO2 coating acted as an efficient barrier against corrosion and reduced the release of metal ions from the Ti–6Al–4V alloy under simulated physiological circumstances. The results also showed that ion release was enhanced with the falling pH levels. In conclusion, the proposed coating showed remarkable biological performance and antibacterial properties and it is expected to improve surface properties and long-term functioning of biomedical titanium implants.

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تحسين الأداء المضاد للبكتيريا لطلاءات المواد الحيوية المتدرجة وظيفيًا على سبيكة Ti–6Al–4V

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الخلاصة:

استُخدمت تقنية الترسيب الكهربائي (EPD) لتحضير طبقات من هيدروكسي أباتيت/ثاني أكسيد التيتانيوم (HAp/TiO_2)ذات تدرج وظيفي مكونة من سبع طبقات على سبيكة Ti–6Al–4V لتطبيقات الزرع الطبي الحيوي. صُممت بنية الطلاء بتدرج تركيبي من ثاني أكسيد التيتانيوم النقي بالقرب من الركيزة إلى هيدروكسي أباتيت النقي على السطح الخارجي، وذلك لدمج مقاومة التآكل لثاني أكسيد التيتانيوم مع التوافق الحيوي لهيدروكسي أباتيت. عُولجت العينات المطلية حراريًا عند 950 درجة مئوية لمدة ساعة واحدة تحت جو من الأرجون لتحسين استقرار الطلاء وتكوين الطور بعد الترسيب.

قُيّمت الخصائص البنيوية للطلاءات باستخدام حيود الأشعة السينية .(XRD) أكدت النتائج وجود هيدروكسي أباتيت، بالإضافة إلى طوري الأناتاز والروتيل من ثاني أكسيد التيتانيوم. علاوة على ذلك، لوحظت أطوار أخرى من فوسفات الكالسيوم نتيجة التحلل الجزئي لهيدروكسي أباتيت أثناء عملية التلبيد. تم تقييم سلوك التآكل باستخدام اختبارات الاستقطاب الديناميكي في محلول رينجر، حيث أظهرت العينات المطلية مقاومةً أفضل للتآكل مقارنةً بسبيكة Ti–6Al–4V غير المطلية. كما تم تقييم النشاط المضاد للبكتيريا ضد بكتيريا الإشريكية القولونية باستخدام طريقة منطقة التثبيط. أظهرت الطلاءات المطورة أداءً فعالاً مضاداً للبكتيريا وقللت من نمو البكتيريا. تشير النتائج إلى أن طلاءات HAp/TiO2 المتدرجة وظيفياً يمكن أن تُحسّن بشكل كبير خصائص سطح سبيكةTi–6Al–4V ، ولها إمكانات كبيرة في تطبيقات الزرع الطبي الحيوي.

الكلمات الدالة:-ثاني أكسيد التيتانيوم، الطلاءات المتدرجة وظيفياً، سبيكة Ti–6Al–4V، هيدروكسي أباتيت، النشاط المضاد للبكتريا، مقاومة التآكل.