Conducting polymeric hybrid implant coating: A strategy to improve electrochemical and osteocompatible properties

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Abstract:

The replacement of entire joint extent is one of the actual effective and common surgical techniques to support both hip as well as knee reconstruction. To cover-up with the mechanical strength and biological effect of in-situ natural bone, titanium is the only material of superior choice. In recent years, conducting polymers provide a complimentary platform as coating material, exclusively for orthopaedic application. Polythiophene derivatives have particular attention and in context poly(3,4-ethylenedioxythiophene) (PEDOT) is considered as the most gainful polythiophene derivative with its outstanding properties. PEDOT is practically used in device production, biomedicine, and bio-implants owing to the peculiar electrochemical and environmental permanency with respect to its oxidation state. The trace salt of gallium element boosts the content of phosphorous and calcium in bone, that in contrast electively serve for hypercalcemias as well. Gallium in hydroxyapatite matrix acts as a shield to improve the skeletal structure and in turn the biomechanical properties. In the current research an effort is made to understand the application of innovative implant with gallium doped PEDOT on titanium for orthopaedic practice. Through primary studies like SEM, EDX and FTIR the presence of predictable layer of PEDOT with Ga was acknowledged. Contact angle, electrochemical corrosion studies and in vitro immersion studies were performed and the outstanding results meet the required physicochemical standards to enrich in loco osteosynthesis.

Keywords: *Titanium; Poly(3,4-ethylenedioxythiophene) (PEDOT); Gallium; Corrosion; Bioactivity; Orthopaedic*

1. Introduction

Bone is exposed to numerous loading situations, sometimes the exposed load could cause cracks or affect the patient majorly [1]. To support such aforementioned problems, a substitute is used that maintain the prime concern and stay compatible with the bone. Biomaterials are observed with an express growth in research field of bone implants. After implantation, the occupied states of implants due to jumping, loading and running for a long term performance could lack the compatibility with original bone. Henceforth, the development of an implant should necessarily focus on mechanical strength and other properties to serve without any knockback [2]. To decrease the second revised surgery, the upgraded techniques have been initiated. Still 26% of failure cases were recorded in the past decade among aged patients. Metals have ensured the dominance for load bearing role in implant field [3]. Among the different metals used in orthopaedic, titanium is the strongest and lightweight metal that plays a critical load bearing function than other medically used implant metals such as cobalt-chromium alloys and steel. This material exhibits excellent biocompatibility that is attributed to the naturally obtained TiO2 layer on the surface. This oxide layer develops an osteoconductive layer with the interface and therefore bone cells get attracted. The surface roughness of titanium influences the growth factors. Thus, remodelling the titanium surface to achieve the roughness in implants provides in site cellular responses for a long time

in implants [4]. The surface coating is an important method to improve the significant performance of titanium.

Different biocompatible polymers are used in biomedical applications, out of that the conducting polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) have similar features to that of melanin. PEDOT polymer is known for its conductivity and chemical and environmental stability. The PEDOT coated surfaces are soft, remain relatively bioactive and protect the material from electrochemical corrosion [5]. Since the coating material is a very important part that provides the improved performance in implants, gallium was doped with PEDOT. The bioactivities such as skeletal metabolism, stress relief and bone resorption are improved with gallium. Plenty of reported cases were published with gallium for treating cancer-based hypercalcemia's and osteoporosis. There are studies proving the antimicrobial activities of the gallium metal. In accordance, gallium ions are gaining significance in medical field with anti-inflammatory, antiresorptive, immune suppressive behaviour and antiosteoporotic behaviour. Gallium is a highly efficient element that works effectively for treating hypercalcemia's [6]. In orthopaedics, gallium hinders the rate of apatite growth by adsorbing into crystal surface therefore, used in various biotechnological performances [7].

Electropolymerization is ordinarily accomplished through three methods such as (i) galvanostatic: performed by maintaining the constant current, (ii) potentiostatic: executed by applying constant voltage and (iii) potentiodynamic: within a definite voltage window, the cyclic voltage gets swept out. Fine tuning of the parameters of electropolymerization method, concentration of the dopant used, solvents and the type of dopant used the morphology, conductivity and thickness of the layer can be precisely controlled [8]. The aim of this research is to electropolymerize a layer of gallium doped PEDOT on titanium metal surface for improving the biological and electrochemical properties of titanium implant for a long term and load bearing application. This is mainly to eliminate the second painful revised surgery to replace the implant.

2. Materials and Methods

Commercial pure Titanium (Cp-Ti) samples sized 15 mm × 20 mm × 2mm acquired from TI Anode Fabricators Pvt. Ltd. Chennai, India were used. The test samples were mechanically polished by silicon carbide (SiC) papers from 80 to 1000 grits. The polished samples were washed with acetone and then with the distilled water.

Cyclic voltametric method was used for the electro-polymerization of EDOT and gallium nitrate on the titanium surface since it is a suitable, cost-effective and an easy process. The electropolymerization was carried out using PGSTAT Autolab-302 N electrochemical workstation by using a three-electrode cell system. Polished titanium substrate was used as working electrode (WE), a saturated calomel electrode was taken as reference electrode (RE) and a platinum foil was taken as a counter electrode (CE) respectively. The electrolyte used for the electrochemical polymerization was prepared using different concentrations of gallium nitrate, 0.3 M lithium perchlorate and 0.1 M EDOT. Poly (3,4-ethylene dioxythiophene) and gallium nitrate were polymerized on titanium surface at a sweeping potential rate between -0.1 and + 2.0 V with a scan rate of 0.03 mVs-1 for 5 cycles. After electro polymerization, the polymer coated substrate was washed with distilled water to eradicate the monomer particles and dried.

2.1. Characterization Techniques

The surface characterization of electropolymerized samples were examined using SEM with EDS (Tescan Vega 3 XMU). The chemical composition of the sample was confirmed through ATR-FTIR (Perkin Elmer Spectrum two, USA). The Contact angle analyser: Phoenix 300 plus was applied to observe the wettability of the samples.

2.2. Electrochemical Corrosion Studies

The potentiodynamic polarization studies were carried out for the samples having an exposed area of 1 cm^2. A conventional three electrode glass cell was used for all the electrochemical measurements. The cell assembly consisted of the test specimen as

the working electrode, a platinum foil as the counter electrode and the saturated calomel electrode (SCE) as reference electrode. The tests were performed in 250 ml Hanks` solution. The electrochemical workstation (PGSTAT model 302N, Meterohm Autolab B.V, Netherlands) was controlled by Nova 2.0 software. Potentiodynamic polarization studies were carried out in the potential range from -1.0 to 1.0V at a scan rate of 0.001V/s. The potentials recorded are with respect to standard calomel electrode. The corrosion current density (Icorr) and corrosion potential (Ecorr) were obtained from the polarization curves. The obtained corrosion current and corrosion potential represents the rate of corrosion of the working electrode. The current density is obtained using Stern – Geary equation given below [9].

$$i_{corr} = \frac{\beta a \times \beta b}{2.3\, Rp(\beta a + \beta b)}$$

Where βa and βb are the Tafel slopes of the anodic and cathodic parts of the Tafel plot respectively and Rp is the polarization resistance.

2.3. *In Vitro* Studies

In vitro studies were accomplished to inspect the apatite progression. The sample was immersed in freshly synthesized Hanks' solution with 7.4 pH. After 7 days of protective immersion, the characterizations such as SEM, and EDX were used to confirm the growth of apatite.

3. Results And Discussion

3.1. Morphological Studies of Ga/PEDOT

The titanium surface was coated with gallium doped PEDOT with different concentrations of gallium nitrate (0.005 and 0.006 M). Higher magnification SEM images of the coatings obtained by means of cyclic voltammetry are shown in Fig. 1. A stable coating of Ga/PEDOT was seen on both the sample surfaces with porous structure that are connected and branched in such a way with gallium oxide on it. In Ga/PEDOT(1), the coating is satisfactorily layered with PEDOT and gallium oxide and in case of Ga/PEDOT(2) the coating was very least coated. The surface should be completely covered and the appearance of random irregular voids provides a beneficial adherence of coatings. The monomers of EDOT have experienced the initial nucleation and fine accumulation with complete polymerization and deposition in Ga/PEDOT(1) on contrast of that of Ga/PEDOT(2) [10]. From the FESEM image, it is evident that the titanium surface is completely wrapped with Ga/PEDOT(1) and therefore, this sample was progressively used in this research.

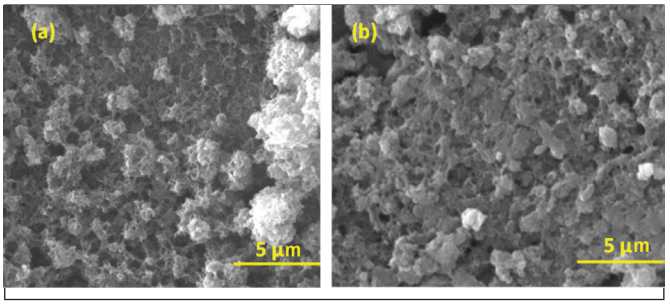
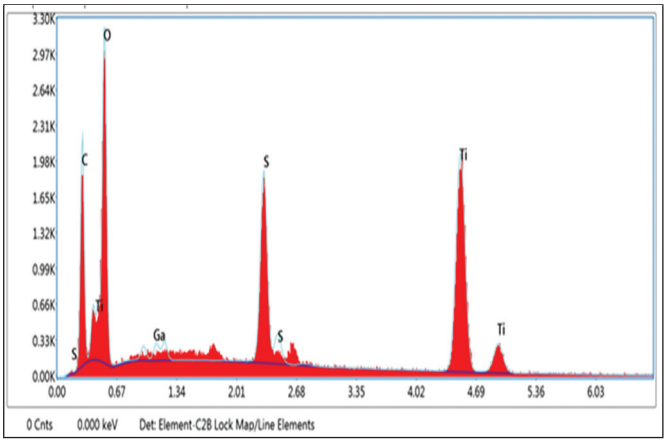


Fig. 1. SEM images of (a) Ga/PEDOT(1) and (b) Ga/PEDOT(2).

The quantitative chemical composition of Ga/PEDOT(1) was obtained through EDX microanalysis. Table 1 shows the relevant most variations of elements present in the implant material. In particular, titanium is the most abundant element with intense peak and Ga is the most minor element as shown in Fig.2. The presence of all essential elements such as Ti, O, C, S and Ga are ascribed to the trend of chemical composition and their presence on the surface of the fabricated implant material.



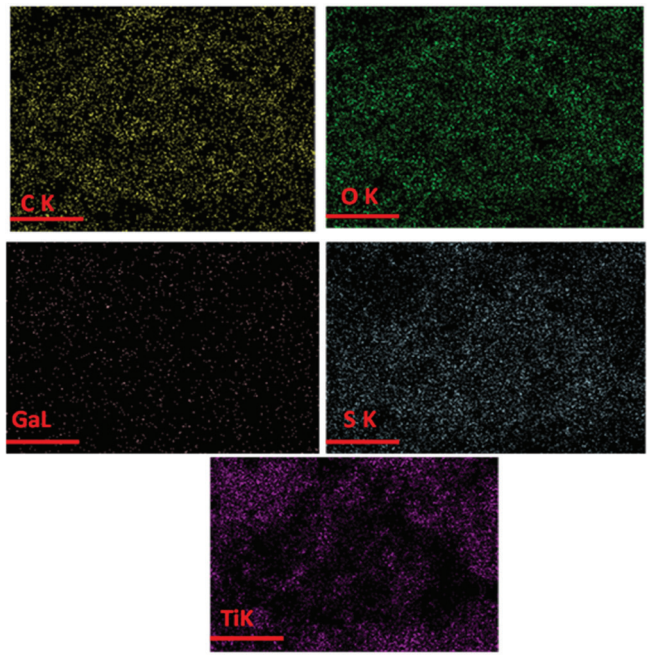


Fig. 2. EDX profile of Ga/PEDOT (1).

Table 1. Parameters obtained from EDX profile of Ga/PEDOT (1)

S.No.	Elements	Weight %	Atomic %	Error %
1.	C K	9.14	20.77	9.22
2.	O K	21.55	36.78	10.50
3.	Ga L	0.95	0.38	8.92
4.	S K	11.07	9.42	3.70
5.	Ti K	57.29	32.65	4.27

3.2. Electropolymerization using cyclic voltammetry method

In cyclic voltammetry of Ga doped PEDOT, both anodic and cathodic scans during the completion of electropolymerization are shown in Fig. 3. Through the anodic reaction, Ga and PEDOT are coated and the coating removal occurs during the cathodic scans. It is a reversible scanning process and both the scans require equal charges and develop a nucleation loop. The monomer EDOT and $Ga(NO_3)_3$ with the support of $LiClO_4$ get coated as Ga/PEDOT on titanium substrate. Technically in the graph, next to the switching potential one can observe that the current at oxidation scan is more than the current produced at the reduction scan that represents the effects of polymer nucleation process. This is the evident that there is a homogeneous connection that occurs within the starting monomer ions and the oligomer products respectively [11].

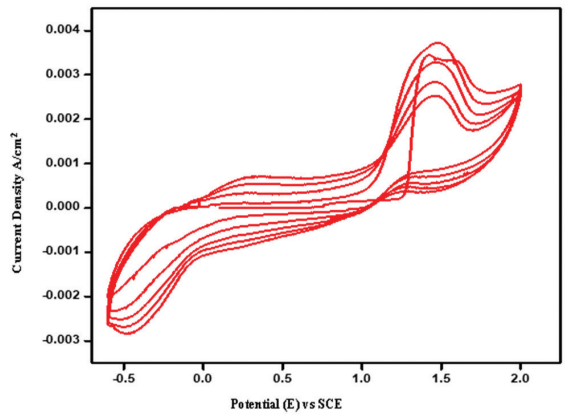


Fig. 3. Cyclic voltammogram curves of Ga/PEDOT (1).

As the coating is an electro active polymer layer, the thickness of the coating increases when the additional crosslinking deponent Ga is used. If the coated layer becomes thicker and bulky, this bulking effect will limit the adhesion towards the titanium substrate. Therefore, a uniform and flat layered coatings of the polymer without any bulking features aids the positive interactions necessary for orthopaedic applications and stay for a long period [12]. For this reason, only 5 scans were accomplished for the successful electropolymerization of Ga/PEDOT on titanium surface.

3.3. ATR-FTIR analysis

To identify the functional groups, ATR-FTIR spectra of bare and Ga/PEDOT(1) were recorded in the range of 450–4000 cm^{-1} (Fig. 4). The bare substrate spectrum shows a dominant peak of titanium at 489 cm^{-1}. The surface of titanium contains its oxide layer and therefore, the oxide formation of titanium is represented through this resultant peak. The spectrum of Ga/PEDOT (1) shows a peak at 495 cm^{-1} which indicates the presence of Ti-O stretching vibrations. The peak obtained at 628 cm^{-1} represents the appearance of stretching vibrations

in Ga-O [13]. A small bend at 811 cm^{-1} is obtained which is attributed to C-S of the thiophene ring. The peak at 1010 cm-1 describes the bending vibration of oxyethylene thiophene ring [14]. At 1329 cm^{-1}, the small peak shows the occurrence of C-C bond and at 1537 cm^{-1} shows the confirmation of alternative C=C bond in the ring structure [15]. The absorption peak at 1818 cm^{-1} is attributed to C-O bond of PEDOT. The peaks at 2050 cm^{-1}, 2240 cm^{-1} and 2647 cm^{-1} represents -CH_2 bond. The formation of –OH group was identified and matched with the peaks at 3199 cm^{-1} and 3799 cm^{-1}. The presence of gallium doped PEDOT was further confirmed through this characterization technique and the possible interactions and bonding were verified.

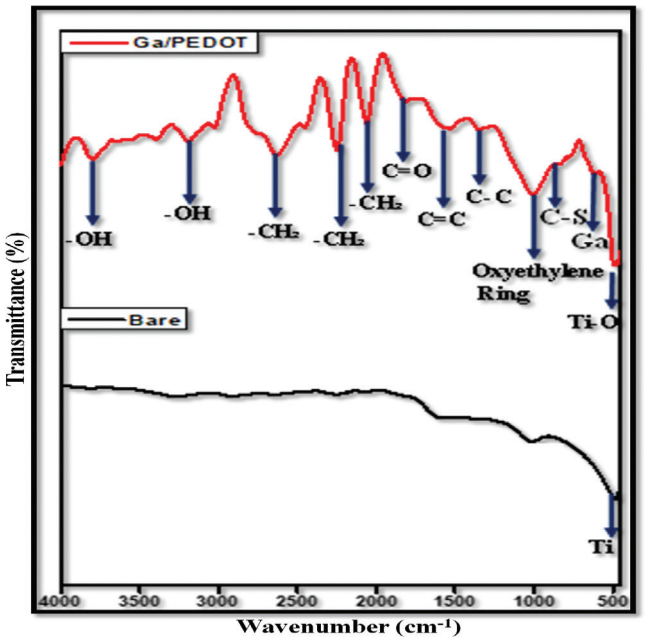


Fig. 4. ATR FTIR of bare and Ga/PEDOT (1).

3.4. Contact angle measurements

Any bio-implant should be studied for its surface wettability to understand the bioactivity including protein adsorption, proliferation and cell adhesion. The wettability of an implant surface are connected with the topography and chemistry of that particular surface [16]. The contact angle measurements were carried out on the Ti substrate and the substrates coated with Ga/PEDOT(1) and Ga/PEDOT(2) and the graphical representation with images are shown in Fig. 5. The roughness found at the metal surface affects the properties and significant structures that develop a live interaction with biological matter [17]. With respect to this, the material surface showing a water contact angle (WCA) greater than 90º is considered scientifically as a hydrophobic one [18]. Therefore, the bare substrate with TiO_2 on the surface exhibits WCA of 104.2º, which is hydrophobic and represents the obstacles in adhesion, migration and growth of cells. The particles gets aggregated into the body fluids and develop weaker cell bonding [19]. In coated samples, the initial oxidized layer has been covered with polymer PEDOT and gallium. Thus, Ga/PEDOT(1) and Ga/PEDOT(2) shows hydrophilicity with the average WCA values were 67.6º and 51.0º respectively. The cell walls in human tend to interconnect and attach with the hydrophilic surfaces for the betterment of growth [20]. More roughness develops the wettability and enhances the cell attachments by the adsorption of required proteins.

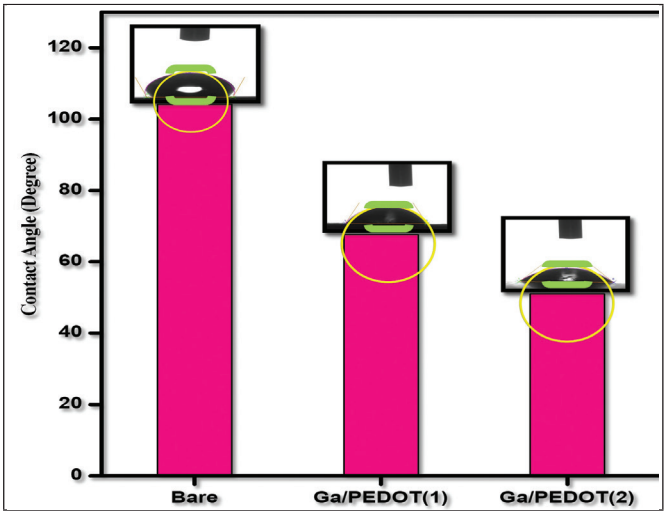


Fig. 5. Contact angle measurements on Ti and coated surfaces.

3.5. Electrochemical corrosion studies

3.5.1. Potentiodynamic polarization studies

The potentiodynamic polarization curves were recorded for bare titanium and Ga/PEDOT(1) coating in Hanks' solution as the electrolyte to assess the corresponding biological activity of the implant. The unique potentiodynamic polarization curves plotted for bare and Ga/PEDOT(1) are shown in Fig. 6 and the respective electrochemical values calculated are summarized in table 2. The corrosion

current density called Icorr value is established from cathodic curves of the graph. The Ecorr value obtained from the graph shows a positive shift in Ga/PEDOT(1) with respect to the bare substrate. This indicates improved corrosion resistance of the titanium surface containing gallium-PEDOT. In the literature it has been reported improved corrosion resistance of gallium and its alloys [21]. The uniform coating of conducting polymer, PEDOT as a passive layer increases the protective mechanism in the corrosive medium [22]. Overall, Ga/PEDOT(1) is a promising coating for orthopaedic applications with respect to corrosion performance.

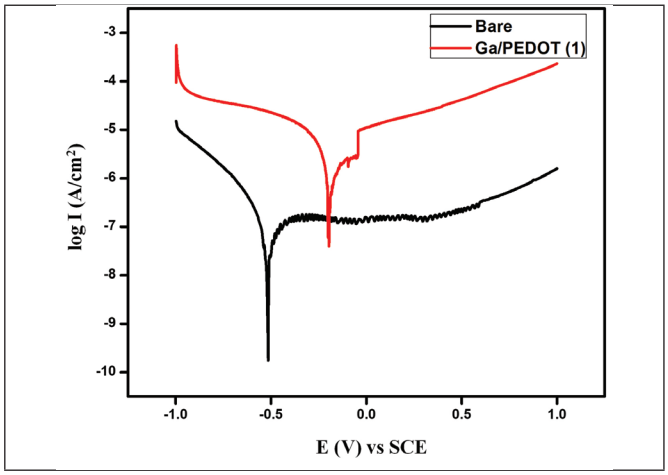


Fig. 6. Potentiodynamic polarization curves of bare and Ga/PEDOT (1).

Table 2: Parameters of potentiodynamic polarization studies

S. No.	Sample	E_{corr} (V)	Icorr (μA/cm²)
1	Bare	-0.515	0.54
2	Ga/PEDOT(1)	-0.194	1.49

3.5.2. Electrochemical impedance spectroscopic studies

An ideal orthopaedic implant material in human body should retain outstanding corrosion resistance against the physiological environment. Electrochemical impedance spectroscopy (EIS) is a very beneficial approach to observe the electrochemical in situ changes. This method helps in understanding the physical deviations happening at the interface of electrode and electrolyte [23]. The obtained results were plotted in the form of Nyquist, Bode phase angle and Bode impedance. The respective graphs of bare and Ga/PEDOT(1) are displayed in Fig. 7. The Nyquist graphs (Fig.7a) shows a higher diameter for Ga/PEDOT(1) than the bare sample. This explains that the more passivity of Ga/PEDOT(1) against corrosion. This is again verified with Bode studies which is a reliable method to gain extracted information about diffusion impedance, rate of charge transfer and its processes, solution resistance and double layer capacitance. The conducting polymer (PEDOT) coatings with low porosity, dense and adherent layer of gallium nitrate maintains a restricted access for the electrolytic oxidants and ions. Here the conducting polymer coating forms a protective layer on the surface of metals, this mechanism is called as anodic protection mechanism [24]. From Fig. 7 (b & c) also shows improved corrosion resistance of Ga/PEDOT(1) than bare material.

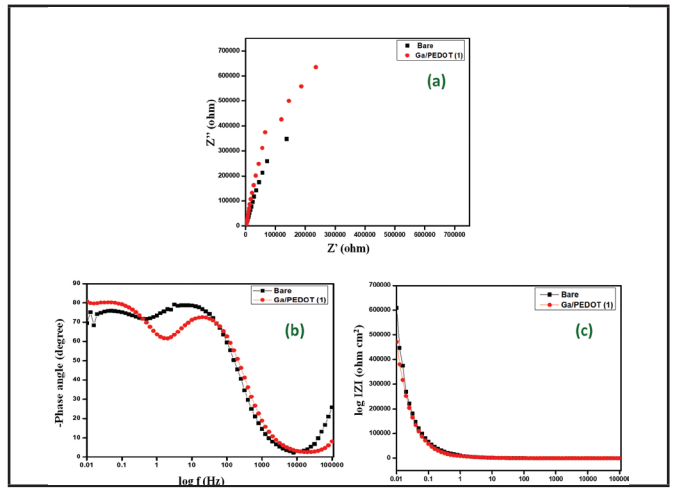


Fig. 7. Electrochemical impedance plots of bare Ti and Ga/PEDOT(1) surface on Ti.

3.6. *In vitro* studies

The biomineralization is a process that provides a bridging the bone-implant with the natural bone. The natural bone of human could get fused with the biomaterial implant and osseointegration takes place. As an initial prediction, the sample was taken for Hanks' immersion test. Ga/PEDOT(1) was soaked in Hanks' solution for 7 days to identify the early bioactivity of the material. After 7 days, the bioactivity of the material depends directly on the amount of apatite induced on the implant surface.

Based on this, the material will be considered as a bioactive one [25]. Fig. 8 shows the SEM image of Ga/PEDOT(1) after 7 days of immersion in Hanks' solution.

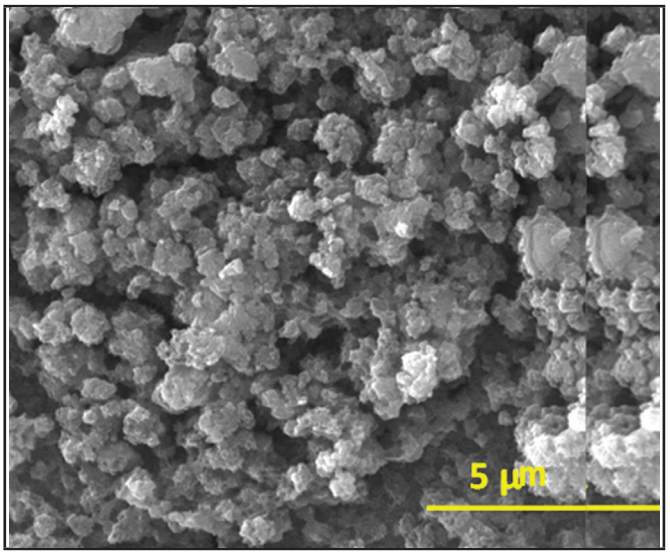


Fig. 8. SEM of Ga/PEDOT(1) after 7 days of Hanks' soaking.

There are few parameters to prominently modify the bone forming aptitude of the biomaterial including roughness, impurity content, crystal size, surface chemistry and morphology [26]. By taking all the above criteria we could match with the apatite growth on the surface through the top view SEM image after 7 days of immersion. The clear growth of hydroxyapatite is layered up as crystalline spherical structures with calcium and phosphate groups on it.

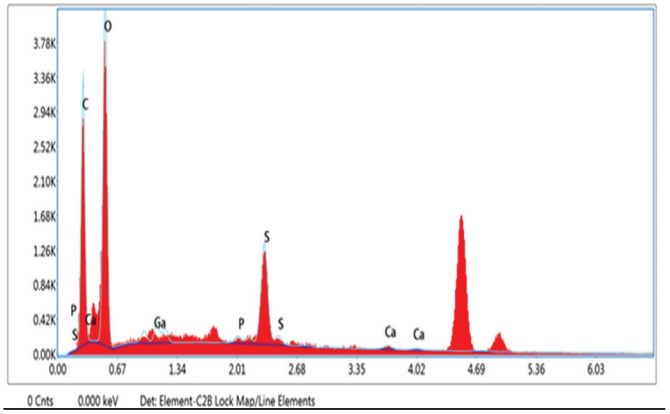


Fig. 9. EDX profile of Ga/PEDOT(1) after 7 days of Hanks' soaking.

The growth of apatite as calcium and phosphate along with the occurrence of carbon, oxygen, sulphur and gallium is verified through EDX (Fig. 9) of Ga/PEDOT(1) after 7 days of immersion respectively. The clear discrimination of the weight percentage in each element is represented through the data given in Table. 3. The total in vitro characterization represents that Ga/PEDOT(1) is biologically active by establishing a positive osseointegration accountable for orthopaedic application that meets up the expectations of the researchers.

Table 3 Elemental analysis of Ga/PEDOT(1) after immersion in Hanks' solution for 7 days

S. No.	Elements	Weight %	Atomic %	Error %
1.	C K	38.11	50.86	9.57
2.	O K	38.28	38.35	8.46
3.	Ga L	3.12	0.72	6.07
4.	P K	1.01	0.52	15.29
5.	S K	17.60	8.80	3.85
6.	Ca K	1.87	0.75	29.22

4. Conclusions

In conclusion, this work examined the improved electrochemical and biological performance of modified polymeric hybrid titanium implant. The surface modification of titanium by the electropolymerization of gallium doped PEDOT was strategically performed at different concentrations of gallium using cyclic voltammetry method. The confirmation of the overlaid coating was verified with SEM, EDX and FTIR. The gallium addition in PEDOT matrix in a very small amount has effectively enhanced the corrosion resistance. The thin degradable layer of Ga/PEDOT on titanium surface ensures the positive attitude towards the biological performance required for osseointegration, determined through immersion studies. This has been correlated with contact angle measurement showing good wettability on Ga/PEDOT(1) surface. In summary, the developed polymeric hybrid implant material containing appropriate amount of gallium improves the patient's expectancy in progressive bone healing (Hip & knee) with titanium base.

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