Semiconductor Optoelectronics, *Vol. 42 No. 2 (2023), 1069-1076*
https://bdtgd.cn/

Semiconductor Optoelectronics
ISSN: 1001-5868

THE EFFECT OF NANOCOMPOSITE MIXTURE OF 70% TIO_2 AND 30% ZRO_2 COATING MATERIAL ON SURFACE FORMATION OF HYDROXYAPATITE LAYER

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ABSTRACT
This study aimed to evaluate the effect of nanocomposite mixture of 70% TiO_2 and 30% ZrO_2 coating material on surface formation of hydroxyapatite layer. Three groups of commercially pure titanium (uncoated and coated with nan composite mixture with 70% TiO_2 and 30% ZrO_2 by electrophoretic deposition and dip technique). The evaluation with simulated body fluid (SBF), thirty discs (10 for each group) were soaking in SBF for 14 days then evaluated by using, optical microscope, atomic force microscope, X-ray diffraction analysis, scanning electron microscope and energy-dispersive X-ray investigations. However hydroxyapatite formation on electrophoretic deposition (EPD) more existing while uncoated samples are the last.

INTRODUCTION

TiO2 and other biomaterial coatings immersed in SBF for a given period of time become covered by a layer of hydroxyapatite (HA) if they exhibit bioactive behavior. Thus the rate of deposition and microstructure of this HA layer on the surface of coatings are commonly used to evaluate the material bioactivity [32]. This simple acellular bioactivity test in SBF was carried out on the present coatings.Titanium dental implants are the most favorable treatment option in replacing the missing teeth, the most important property in succeeded dental implant is new bone formation at implant bone interference (osseointegration) (Abrahamsson and Cardaropoli 2007)., Titanium is a material of choice (Rupp *et al.,* 2018), coating of CpTi discs with nanocomposite mixture of 70% TiO_2 and 30% ZrO_2 have been studies in increase surface roughness. The SBF can be used as an *in vitro* testing method to study the formation of apatite layer on the surface of implants so as to predict the *in vivo* bone bioactivity (Chen et al., 2008).

Sample preparation:

Commercially pure Titanium (grade 2) was cut into small circular discs (20 mm diameter and 1 mm thickness) with a lathe machine which used as the substrate for coating and then used for socking in SBF. After polishing and cleaning of samples, coating with nanocomposite mixture of 70%TiO_2 and 30% ZrO_2 by EPD and dip techniques (Zwain & Hamad, 2018).

Simulated body fluid bioactivity :

First step: Preparation of simulated body fluid.

The solution was prepared by dissolving reagent-grade NaCl, KCl, $NaHCO_3$, $MgSO_4$. 7 H_2O, $CaCl_2$ and KH_2PO_4 into deionized water using hot plate stirrer with a magnetic stirring facilities. The samples were soaked in a concentrated SBF, the concentration of the salts was 5 times than that found in human blood plasma (Chen et al., 2005; Habibovici et al., 2005). Ion concentration of the SBF and blood plasma seen in Table (1).

Table (1): Ion concentrations of the SBF and blood plasma.

Ion	Ion concentrations (mM)	
	Blood plasma	SBF
Na^+	142.0	142.0
K^+	5.0	5.0
Mg^{2+}	1.5	1.5
Ca^{2+}	2.5	2.5
Cl^-	103.0	147.8
HCO^{3-}	27.0	4.2
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5
pH	7.2-7.4	7.4

After complete dissolution, the solution was buffered at pH=7.3 with NH_4OH and HCl at 37°C (Baker et al., 2006).

Second step: the samples were soaked in a concentrated SBF. Three groups of discs (uncoated, EPD and dip coating) each group have 10 samples were immersed in SBF vertically on Teflon plate in plastic container, 400 mL of SBF in each container refresh every week. After 14 days the samples washed in deionized water and dried for subsequent analysis (X-ray diffraction, atomic force microscope, and scanning electron microscope) were taken to evaluate the bioactivity of each group of discs.

Result

Atomic force microscope(AFM) findings

The surface topography analysis including surface roughness analysis were provided by the atomic force microscope for the three groups (control, EPD and dip coated samples) before and after 14 day soaking in SBF. AFM analysis shows peaks and projections with the average roughness, average grain size and the granulation distribution charts of the sample . As shown in Figures (1, 2, and 3)

soaking

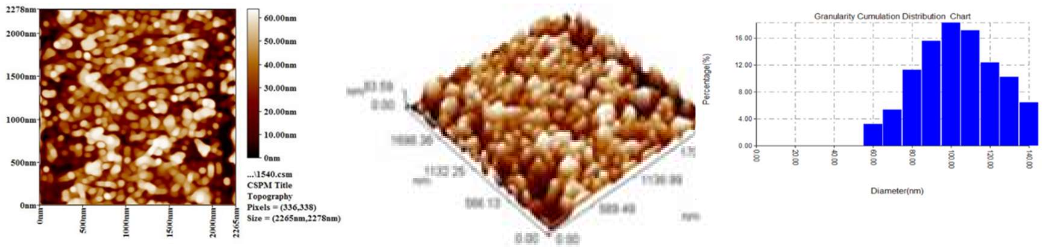
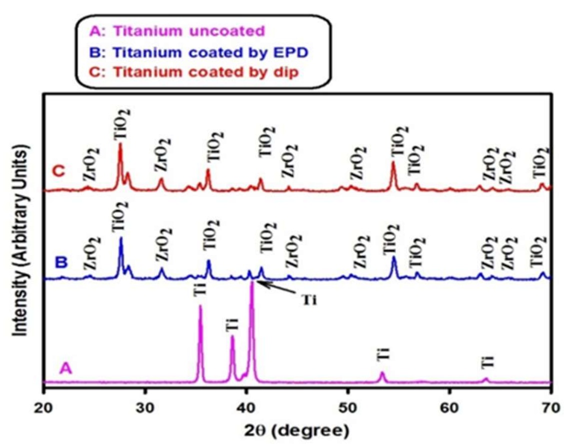


Figure (2) AFM topographies and granulation distribution charts of the EPD coated surface with nanocomposite mixture of 70%$TiO_2$and 30%ZrO_2 after 14 days soaking in SBF.

Figure (3) AFM topographies and granulation distribution charts of the dip coated surface with nanocomposite mixture of 70%$TiO_2$and 30% ZrO_2 after 14 days soaking in SBF.

X-ray Diffraction analysis:

The results of X-ray diffraction patterns of the three group shown in figure (4). The peak was indexed according to the JCPDS (joint committee on powder diffraction standards) International Centre for Diffraction Data, ICDD file # 44-1294 for titanium, #21.1276 for TiO_2 and #37-1484 for ZrO_2. After 14 days immersion in SBF additional file will appear, #09-0432 for HA according to JCPDS file were the strongest peaks at 2Ө : (27,3), (31,9), (45,4) degrees. As shown in figure (4)



X-ray diffraction of three group. Figure (4):

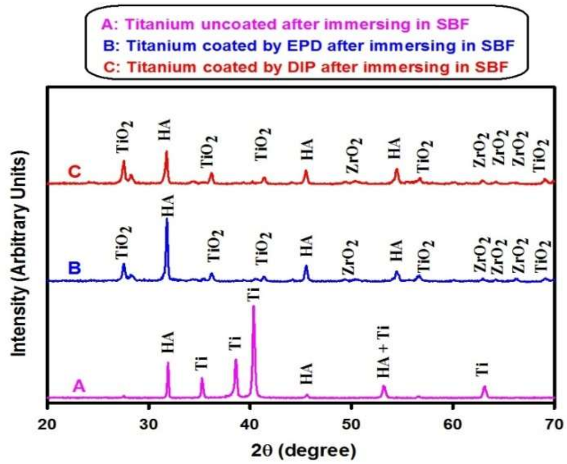


Figure (5): x-ray diffraction of three group after 14 days soaking in SBF.

Scanning electron microscope (SEM) analysis:

Field emission scanning electron microscope (FESEM) at different magnification was used for morphological analysis of CP Ti discs (uncoated, coated by EPD and dip coating) before and after immersion in SBF.

In the FESEM micrograph of uncoated disc showed appearance of HA particles scattered on disc surface after immersion in SBF for 14 days as seen in Figures (7 and 8). In coated discs, there are many irregular projections, and the picture of the surface had a feature or a structure nanoTiO_2 and nanoZrO_2 partials in coated disc, after 14 days of immersion in SBF, the discs showed additional structure on coated disc surface which is amorphous HA particles as seen in figure (9, 10, 11 and 12).

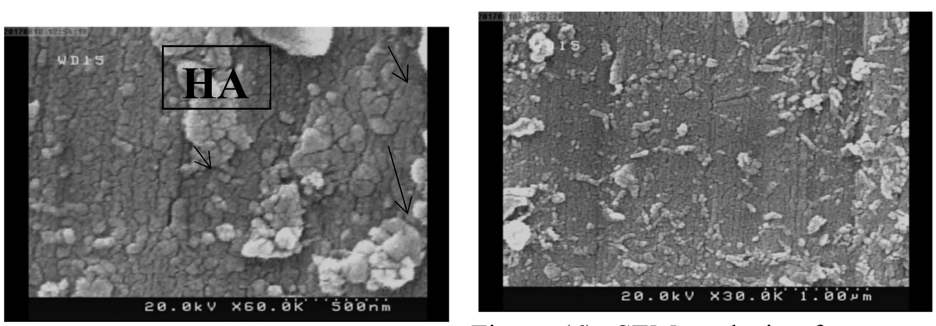
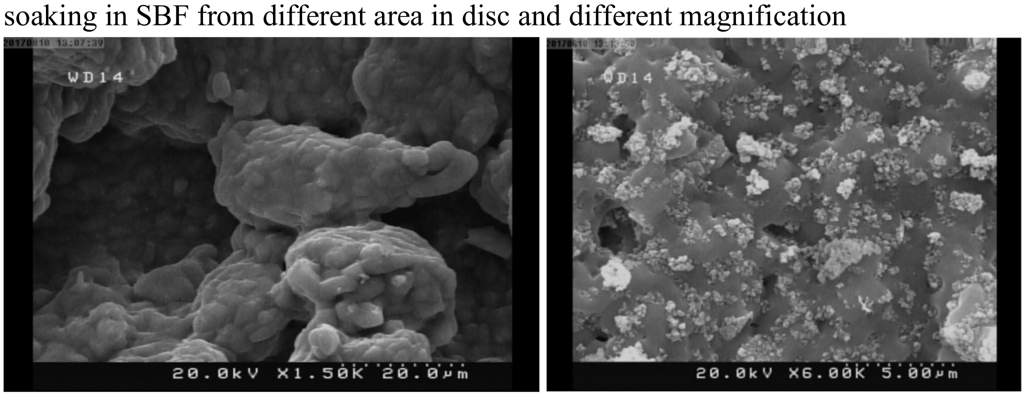


Figure (6): SEM analysis of un coated discs after soaking in SBF from different area in disc and different magnification



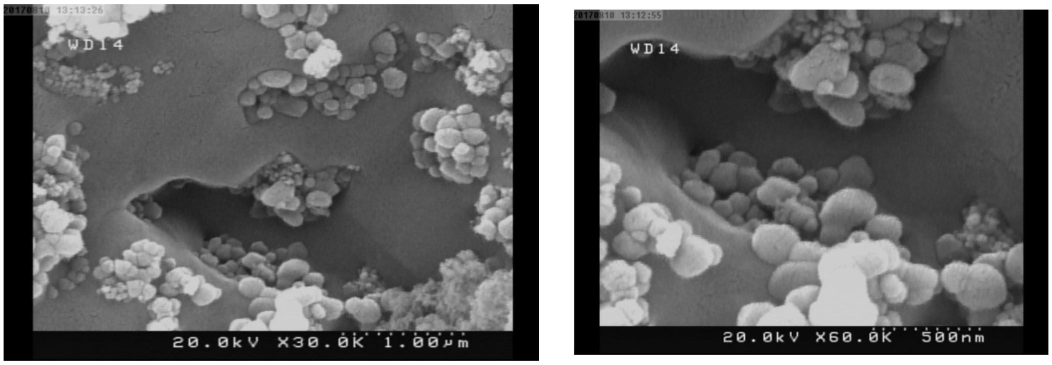


Figure (7): SEM analysis of EPD coated disc after 14 days soaking in SBF from different area in disc and different magnification

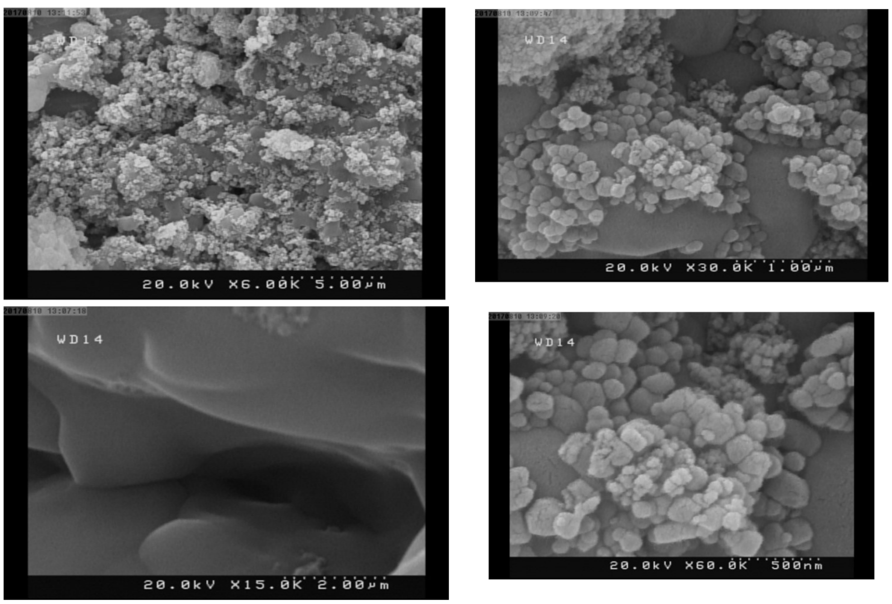
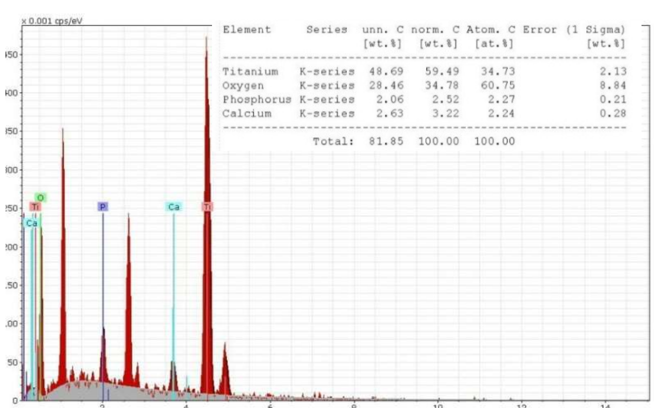


Figure (8): SEM analysis of dip coated disc after 14 days soaking in SBF from different area in disc and different magnification.

Energy Dispersive X-ray spectroscopy (EDX) analysis

EDX analysis for the main Components of the experimental groups on CP Ti discs (uncoated, EPD and dip coating techniques) after immersion in SBF, shows the surface chemical composition including weight and atomic percentages of the main elements, are shown in Figures (13, 14 and 15).



Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Titanium	K-series	48.69	59.49	34.73	2.13
Oxygen	K-series	28.46	34.78	60.75	8.84
Phosphorus	K-series	2.06	2.52	2.27	0.21
Calcium	K-series	2.63	3.22	2.24	0.28
	Total:	81.85	100.00	100.00	

Figure (9): EDX analysis plot for uncoated CP Ti disc after 14 days soaking in SBF.

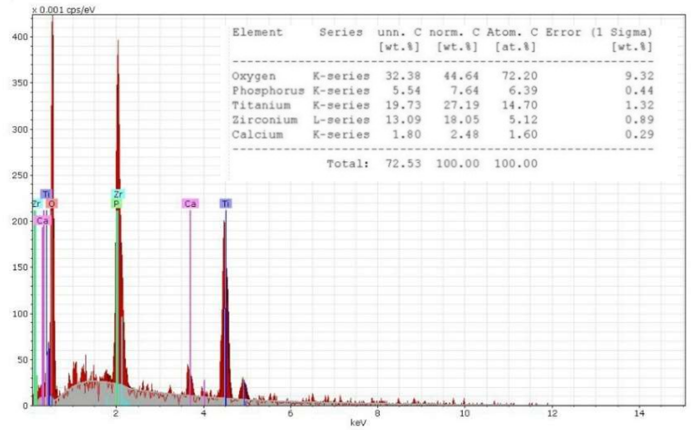


Figure (10): EDX analysis plot for EPD coated CP Ti disc after 14 days soaking in SBF.

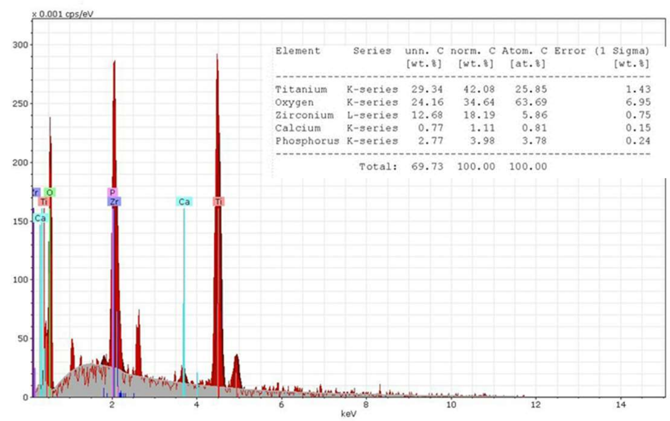


Figure (11): EDX analysis plot for dip coated CP Ti disc after 14 days soaking in SBF

DISSCUSION

Simulated body fluid bioactivity:

The type and crystal size of Calcium phosphate that formed from SBF are largely dependent on the conditions of synthesis, i.e., presence of seeds, the degree of super saturation, ionic strength, the immersion time, solution pH, temperature, etc. all are known to affect the course of synthesis of Calcium phosphate bio ceramics from SBF Macask *et al.,* (2005); Thair *et al.,* (2011).

In this study, the consequences achieved from using a 5 times concentrated SBF in order to accelerate the formation of Calcium phosphate as stated by Oliveira *et al.,* (2002); Chen *et al.,* (2005); Habibovic *et al.,* (2005). The magnesium and carbonate were added to control the size and crystallinity of the deposited layer, both inhibitors of crystal growth, may be adjusted for optimal attachment of coating and formation of a uniform, strong and wear resistant layer while addition sodium chloride and other salts to maintain the ionic strength of the coating solution (Gross and Berndt, 2002; Layrolle *et al.,* 2006).

The uses of 37ºC temperature in SBF solution in order to simulate the degree of body temperature and provide better quality of SBF as shown in the results of Baker *et al.,* (2006), Thair *et al.,* (2011). The pH range from 7.3-7.4 was also used to simulate the same condition of apatite formation inside the After 14 days immersion in SBF the disc surface shown other peaks according to JCPDS file # 09-0432 for HA.

As XRD shows that the narrower peaks are indicative of layer consists of highly crystalline form, while broad peaks represent lower levels of crystallinity, this come in agreement with (Gruene, 2014).

Coating of titanium surface with nanocomposite mixture TiO_2 and ZrO_2 enhance the bioactivity of surface due to the role of bioactive hydroxyl groups (i.e., Ti–OH and Zr–OH) where groups were created by hydration with H_2O on the TiO_2 and ZrO_2 coating surface and by the defect reaction between oxygen vacancies and H_2O, this reaction will result in presence of large amount of hydroxyl groups that lead to a negatively charged surface , thus attracting calcium ions and subsequent $HPO4^{2-}$ in SBF solution to form the apatite nucleus on the coating surface (Popat et al., 2007; Wang, G., 2011) who describe the mechanism by which the nanostructure enhanced the bioactivity (in vitro apatite formation) was proposed in combination with the role of bioactive hydroxyl groups (i.e., Ti–OH).

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