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Synthesis of Al-doped Nano Ti-O scaffolds using a hydrothermal route on Titanium foil for biomedical applications

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ABSTRACT

Al-doped and undoped Ti-O nanowire scaffolds were fabricated on the surface of titanium foil via a one-step hydrothermal reaction in the presence of an alkali solution at 120 ± 1 °C temperature and at 15 psi pressure. Grazing Incidence X-Ray and electron microscopy analyses confirmed that the phase composition, length and diameter of the nanowires depend on alkali concentration and reaction time, and the Al doping. Whereas, Al doping retarded the oxide phase formation and transformation rate and changed the morphology of the nanowires. Preliminary hemolysis test showed better biocompatibility of the Al-doped scaffolds compared to the undoped ones.

1. Introduction

Titanium is considered as an efficacious biomaterial (bone implant, stent) because of its lower specific weight and anti-corrosive property [1]. But, the poor bone tissue adherence and insignificant proliferation on the smooth metallic surfaces originated the need for surface modification of those metallic surfaces. Among the various surface modification techniques mentioned in the literature for Ti [2], in many cases, either the smooth coatings on the metallic surfaces lack the porous structures to accommodate growth-proliferations or the typical natural extracellular matrix is too fragile to support weight. It is believed that the titanate- and TiO_2-based nanowires/nanotubes (NWs/NTs) engineered on the titanium surface can improve the biocompatibility of the metallic surface by providing the proper morphological structure to adhere the cell/tissue and at the same time by administrating enough physical strength to the bioscaffold coating to sustain the tissue growth and proliferations [3–6]. Nano alumina itself is used in bone implantation, and other biomedical applications [7]. Recently, researchers reported application of Al-doped TiO_2 in photocatalysts, photovoltaic, and optoelectronic fields, where Al^{3+} ion substituted Ti^{4+} in TiO_2 lattice structure, which resulted in a decrease in porosity and roughness of the matrix and refined crystallite size of the film significantly [8–10]. There are several examples of different approaches used by the researchers to fabricate Al-doped TiO_2 powder or film by simultaneous RF and DC magnetron sputtering [11], sol–gel method [10], ball mill method [12], and atomic layer deposition [13].

Here, for the first time we report about the synthesis of Al-doped Ti-oxide nano-scaffold on Ti surface by an easy, economical, one-step hydrothermal approach. In order to examine the biocompatibility of the scaffold coating preliminary hemolysis testing was performed. This progress enables us to develop a new solution based synthetic strategy for making important biocompatible nanomaterials and nanodevices.

2. Experimental procedures

2.1. Synthesis of the nanofibre scaffolds

Ultrapure Titanium Foil (99.94% pure on metal basis, thickness 0.025 mm) was cut into 15×15 mm^2 pieces. The pieces were washed in acetone at room temperature, ultrasonically cleaned and rinsed with deionized (DI) water. Subsequently, the clean pieces of the Ti foil were relocated into autoclavable polypropylene bottles each holding 10 ml freshly prepared aqueous NaOH solution with varying concentration ranging from 1 mol/L to 3 mol/L.

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Table 1
Experimental conditions and corresponding scaffold thickness and elemental compositions of the surfaces as obtained from EDX.

Sample name	Alkali conc. (M)	Treatment time (hour)	Scaffold Coating			Al (at%)	Ti (at%)	O (at%)
			Av. Scaffold thickness (nm)	Av. Nanowire dia. (nm)	Av. Nanowire length (nm)			
S0	0	0	NA	NA	NA	NA	100	NA
S1	1	1	180	20	230	NA	30.00	70.00
S2	1	2	320	32	390	NA	28.00	72.00
S3	2	2	460	50	500	NA	28.00	72.00
S4	2	3	600	80	650	NA	27.80	72.20
S5	1	1	165	5	300	0.41	26.00	73.59
S6	1	2	290	12	435	0.94	25.50	73.56
S7	2	2	430	20	750	1.57	24.40	74.03
S8	2	3	550	30	840	2.32	24.00	73.68

After a hydrothermal treatment at 120 ± 1 °C for 1–4 h at 15 psi, the product was washed with DI water, and dried in air. For Al doping 250 mg anhydrous sodium aluminate ($Na_2O \cdot Al_2O_3$, Sigma Aldrich, $>95\%$), was mixed with the NaOH solution during hydrothermal treatment. Table 1 summarizes different treatment conditions (alkali concentration and time) and the corresponding sample designation.

2.2. Characterizations

The phase compositions of the samples were studied using Grazing Incidence X-Ray Diffraction ((GIXRD), Philips X'Pert Pro MRD) at a glancing angle of 0.5°. Morphology, proliferation and composition were investigated with the help of a Field Emission Scanning Electron Microscope (FESEM, Zeiss Supra 40) with Energy Dispersive X-ray Spectroscopy (EDX) attachment.

2.3. Biocompatibility tests/Hemolysis test

Blood compatibility of the samples was estimated by hemolytic activity measurement (details have been described elsewhere) [14]. 10 ml of fresh human blood, collected in a heparinized tube was subsequently centrifuged, washed, and diluted with Alsever solution to achieve the erythrocyte suspension. Afterwards, 0.2 ml of erythrocyte suspension was added into a microfuge tube containing sterilized Ti sample with 10 ml Alsever solution and was incubated for 60 min Finally, the suspension was centrifuged at 3000 rpm for five minutes. A spectroscopy instrument (Micro plate Reader, Bio Rad Model 550) was used to measure the absorbance (at 545 nm) of the supernatant fluid. The Hemolysis ratio was calculated from the following formula [15].

$$HR(\%) = (X_s - X_n)/(X_p - X_n) \times 100$$

Where: X_n, X_s, and X_p, are the absorbance of negative control (a mixture of 0.1 ml erythrocyte suspension and 5 ml Alsever solution), sample supernatant, and positive control (a mixture of 0.1 ml erythrocyte suspension with 5 ml DI water), respectively. The positive control and the negative control indicate 100% hemolysis and 0% hemolysis, respectively. A polished bare surface Ti foil (S0) was characterized simultaneously for comparison.

3. Results and discussion

3.1. Phase analyses

Fig. 1 revealed the GIXRD spectra of the undoped (S2 and S4) and Al-doped (S6 and S8) oxide coatings grown on the Ti surface. Peaks at 35.09, 38.42, and 40.17° are originated from Ti sheet (JCPDS 00-044-1294) and are present for all samples, however the intensity decreases with increase in alkali concentration and

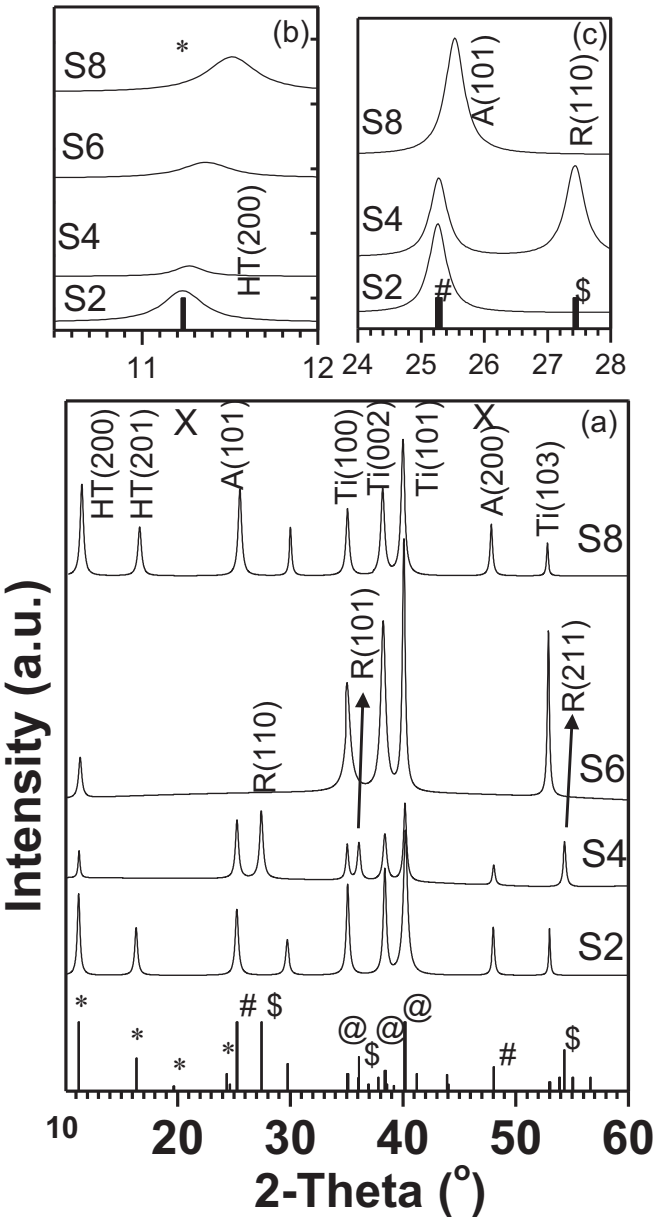

Fig. 1. GIXRD spectra of the coatings grown on Ti surface: (a) S2 and S4 are for undoped coatings and S6 and S8 are for Al-doped coating. Both S2 and S6 are treated at 1M2H and both S4 and S8 are treated at 2M3H, respectively. The bars at the bottom stand for the PDF files of the Ti-O phases;* for $H_2Ti_3O_7$ (JCPDS 00–047–0561), # for anatase (JCPDS 00-021-1272), $ for rutile (JCPDS 00–021–1276), and @ for Ti (JCPDS 00–044–1294). (b) and (c) show the high angle shift of the 100% (200) peak of the $H_2Ti_3O_7$ and 100% (101) peak of the anatase phases for the doped samples. The letters used in the figure (a) mean as follows; HT - hydrated trititanate ($H_2Ti_3O_7$), A-anatase, R-rutile, Ti-titanium.