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Anatase/rutile dual layer deposition due to hydrolysis of titanium oxysulfate with hydrogen peroxide solution at low temperature

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Abstract Anatase/rutile dual layers were deposited on titanium and polyethylene substrates when they were soaked in $TiOSO_4/H_2O_2$ solution and aged in hot water: The dense bottom layer predominantly consisted of rutile, while the upper layer consisted of loosely packed aggregation of anatase particles. The titania deposition was the results of compromise among three conflicting processes: (1) hydrolysis of $TiOSO_4$ to yield either soluble titania-H_2O_2 complexes or titania, (2) dissolution of the titania layer under the presence of H_2O_2, and (3) corrosive reactions between titanium substrates and H_2O_2 to yield similar complexes or compounds. The dissolution–deposition equilibrium was found associated with pH of the sulfate solution and changed with soaking time. Thus, proper pH value and soaking time in the treating solution were the two key factors to control the formation of dense titania layers. The resulted titania layers were easily covered with fine apatite particles when soaked in a solution supersaturated with its component ions.

Introduction

Several oxides derived through specific chemical routes induced formation of apatite, including silica [1, 2], niobium oxide [3], or titania [4–11], when they were soaked in a simulated body fluid (SBF) of the Kokubo's recipe [1]. SBF contains the same inorganic ions as the human blood plasma with similar concentration, and is supersaturated with apatite component ions. Such specific property is denoted as ''in vitro bioactivity'', or sometimes ''bioactivity'' in a simple manner. Those materials are expected to be connected to bone tissues via an intervening apatite layer that spontaneously deposits when in contact with bone tissues. When the bone-material connection is confirmed under in vivo conditions, then, such materials are denoted as ''in vivo bioactive''. By virtue of their mechanical strength or biological and chemical stability, titanium and titanium alloys are common for biomedical implants, and various surface modifications have been attempted to enhance bone induction and conduction [4–11]. Many methods employ strong chemicals or require heating at relatively high temperatures, e.g., above 500 °C. Such heating reduces the amount of M-OH groups (M: metals like Si or Ti) in the surface layers that are considered to favor apatite deposition [2, 12].

Apart from such practical importance, preparation of titania is very much interesting since titania exhibits polymorphism (actually, anatase, rutile, and brookite), and the phase precipitated is highly dependent on the preparation process. A few groups employed low-temperature procedure. Seo et al. [13, 14] prepared anatase via a sol-gel rout, followed by hot water aging. Wu et al. [15] indicated that amorphous titania, derived by corrosion of Ti with H_2O_2 solution containing Ta (V), was crystallized to either anatase or rutile by aging in hot water. They also pointed

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out the importance of dissolution equilibrium of titania and concentration of Ti (IV) in the surrounding medium. Shimizu et al. [16] deposited anatase films on a few substrates using acidic solutions of TiF_4 near room temperature. Recently, Yao et al. deposited a titania layer on polymer substrates due to anion-exchange among borate ions and titanium hexafluoride ions [17] though it took several days for apatite to deposit in SBF. Those techniques seemed versatile for synthesizing bioactive TiO_2 films on variety of substrates since all reactions took place at low temperatures (<100 °C). Indeed, Wu et al. [15] confirmed apatite deposition on their TiO_2 layers as soaking in SBF. However, our preliminary experiments on deposition of titania layers derived from hydrolyzing TiF_4 indicated that residual F^- ions in the titania layers suppressed apatite-forming ability, and that the layers could not induce apatite deposition when soaked in SBF even over 2 weeks. Thus, for earlier deposition of apatite on Ti substrates, not only the increase in the concentration of Ti (IV) in the depositing solution but also absence of moiety like fluoride ions that retard apatite deposition is essential.

Once a low temperature process is developed to fabricate bioactive titania, the process would be applicable to yielding such layers even on organic substrates or to integrating the titania and organic molecules. The bonding between the depositing titania and polymer surface could be enhanced by applying some coupling agent that are chemically active to both materials. Recently, Xiao et al. [18] prepared titania thin films consisting of anatase and rutile deposited on Ti substrates when they soaked the substrates in $TiOSO_4$ solution in H_2O_2 solution and subsequently aged in hot water. Those titania layers proved in vitro bioactive to deposit apatite under body environment, i.e., in SBF.

In the present study, the titanium and polyethylene (PE) substrates were chemically treated at 80 °C with a little $TiOSO_4$/ H_2O_2 solution with varied pH ($TiOSO_4/H_2O_2$ treatment) and subsequently aged in hot-water (80 °C) to obtain bioactive titania layers. The effects of pH and the soaking time in the $TiOSO_4/H_2O_2$ solution were investigated.

Materials and methods

A clear and stable 0.03 M $TiOSO_4$ solution was prepared at room temperature by dissolving reagent grade $TiOSO_4$ (Nacalai Tesque Inc. Kyoto, Japan) in 0.03 M H_2O_2 solution. In fact, this solution was an equimolar mixture of $TiOSO_4$ and H_2O_2. A sheet of commercially available pure titanium (Nilaco Corp., Osaka, Japan) and a sheet of polyethylene (PE) were cut into pieces of $10 \times 10 \times 0.1$ mm^3 in size, and ultrasonically washed with ethanol for 5 min and then with distilled water for another 5 min. The washing cycle was repeated three times. Then, those as-cleaned substrates were divided into two groups: they were named group (pH) and group (ST). The substrates of group (pH) were soaked in 10.0 ml of the 0.03 M $TiOSO_4$ solution at 80 °C for 24 h whose pH was adjusted to 0.58, 0.98, 1.30 and 1.62 with nitric acid. On the other hand, the substrates of group (ST) were soaked at 80 °C for 15 h, 18 h, 21 h and 24 h in 10.0 ml of the 0.03 M $TiOSO_4$ solution with pH being adjusted to 1.30. Those substrates of both groups were ultrasonically rinsed with distilled water, and subsequently aged in water at 80 °C for 3 days. Then, a few scratches were drawn on the PE samples with a needle in order to observe the morphology of the deposited layers and to discriminate the titania layer from the original PE substrate surface. All samples were finally soaked in Kokubo's SBF at 36.5 °C for 1 day. These samples were characterized with an X-ray diffractometer (TF-XRD; RAD IIA, Rigaku, Japan), operated at 30 kV-20 mA acceleration, with a thin-film attachment and observed under a scanning electron microscope (SEM; JEOL JSM-6300, Japan) after their surfaces were coated with gold film.

Results

Group (pH)

As the substrates were soaked in the 0.03 M $TiOSO_4$ solution, pH of the solution changed as listed in Table 1, where pH_i denotes pH for the solution without those substrates, while pH_{Ti} and pH_{PE} denote pH of the solution after the titanium and PE substrates are soaked at 80 °C for 24 h. It is indicated that pH decreased when the substrates were soaked, regardless of the substrate or the initial pH.

Figure 1 shows the X-ray diffraction patterns for the titanium substrates after the $TiOSO_4/H_2O_2$ treatment for 24 h with the solution having the varied initial pH (pH_i). Here, the ultrasonic rinsing drastically changed the XRD profiles. Anatase and rutile were detected on all substrates regardless of pH_i and ultrasonic rinsing, while their relative fraction depended on pH_i of the samples. The TF-XRD

Table 1 Decrease in pH in the treating solution. pH_{Ti} and pH_{PE} denote pH of the solution after each substrate, Ti and PE, was soaked at 80 °C for 24 h in the solution with pH_i

Treating period/substrate	pH values			
0 h (pH_i)	1.62	1.30	0.98	0.58
24 h/PE (pH_{PE})	1.32	1.08	0.84	0.49
24 h/Ti (pH_{Ti})	1.32	1.04	0.74	0.45

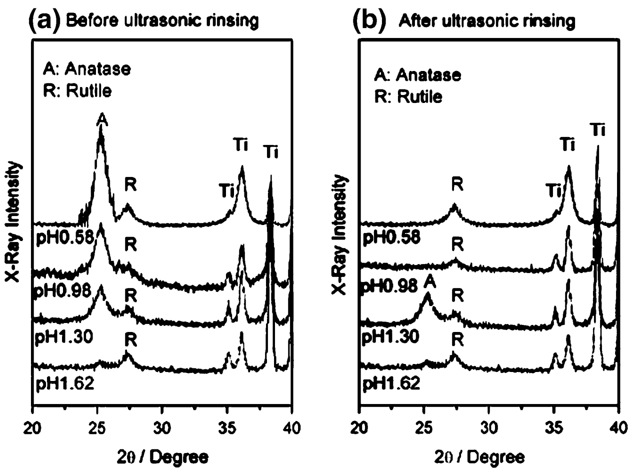

Fig. 1 X-ray diffraction patterns for the titania layers deposited from the $TiOSO_4/H_2O_2$ solutions with varied initial pH_i on titanium substrates. Treating period: 24 h. (**a**) Before and (**b**) after ultrasonic rinsing

patterns in Fig. 1 show that lower pH_i yielded greater intensity of anatase for the samples before ultrasonic rinsing. However, with ultrasonic rinsing the strong anatase diffraction disappeared except for the titania layer deposited under pH_i 1.30. The total X-ray diffraction intensity of each sample indicates that the solution with pH_i 1.30 was optimum because greater amount of titania remained on the Ti substrate after the ultrasonic rinsing. In contrast, the XRD profiles in Fig. 2 for the PE substrates indicate that lower pH_i (0.98) favored deposition of rutile and anatase on PE, though less amount (weaker XRD diffractions) of titania remained on PE than on Ti, when compared among the samples for the same pH_i. The SEM photographs in Figs. 3 and 4 compare the effects of pH_i on the morphology of the titanium and PE substrates, respectively. The darker structure-free area in Fig. 4 indicates the PE surface where the titania layer was scratched off. It is indicated that the titania deposited on either substrate in two forms: one is a thin bottom layer, and the other is in the shape of globular particles or pointed-sugar balls. The bottom layers look dense without apparent pores. From TF-XRD patterns, the titania layers consisting of both rutile and anatase had good bioactivity since they formed apatite in SBF within 1 day (not shown in the present paper). The observation above is summarized as: regardless of the treating conditions, all samples, both Ti and PE, had globular particles comprised the second layer, being spreaded on the bottom solid-dense layer. Here, the morphology of the globular particles was much different from one sample to another; hence, microstructure of the surface layers was very much dependent on pH_i.

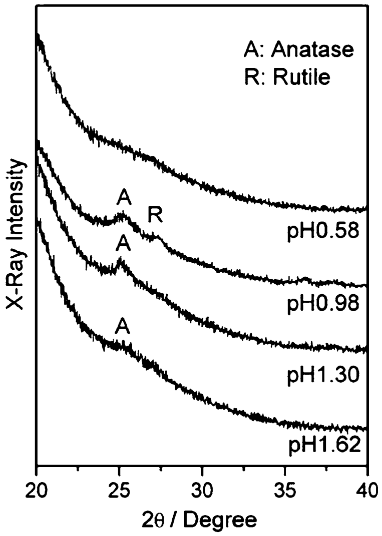

Fig. 2 X-ray diffraction patterns for the titania layers deposited on PE due to the $TiOSO_4/H_2O_2$ treatment with varied initial pH_i after ultrasonic rinsing. Treating period: 24 h

Group (ST)

Soaking time also affected the titania deposition, morphology, and rutile-anatase ratio in the titania layer. Figure 5 shows their surface morphology of the titanium specimens with varied treating time ($pH_i = 1.30$) after ultrasonically driving out the loosely bound particles. After being soaked in the $TiOSO_4/H_2O_2$ solution for 15 h, tiny particles were found to cover the whole surface and form a layer which consisted of both anatase and rutile as the major and minor phase, respectively (from the XRD intensities, not shown here). After 18 h, the particles were agglomerated in bur-like crystallites that had the same morphology as found in Fig. 3c. Though not shown here, the TF-XRD patterns were similar to those in Fig. 1, and the XRD intensity change due to ultrasonic rinsing in a way similar to that demonstrated in Fig. 1. This indicates that the bottom layer was rutile and the particles were anatase. Figure 5(c) shows the surface morphology after moderate ultrasonic-rinsing the specimen with the treatment for 21 h, while Fig. 5(d) shows the surface after sufficient ultrasonic rinsing the specimen treated for 24 h. Note that the particles like agglomeration of burs, found in Fig. 5(b), were present beneath many globular particles with smoother surface, while such globular particles were scarce in Fig. 5(d), and that the bur-like particles found in Fig. 5 (d) were larger than those in Fig. 5(b).

Figure 6 shows the surface morphology of the PE substrates subjected to the same treatment as the titanium ones ($TiOSO_4/H_2O_2$, 80 °C, pH 1.30, ~24 h). The dark area corresponds to the one from which the titania layer

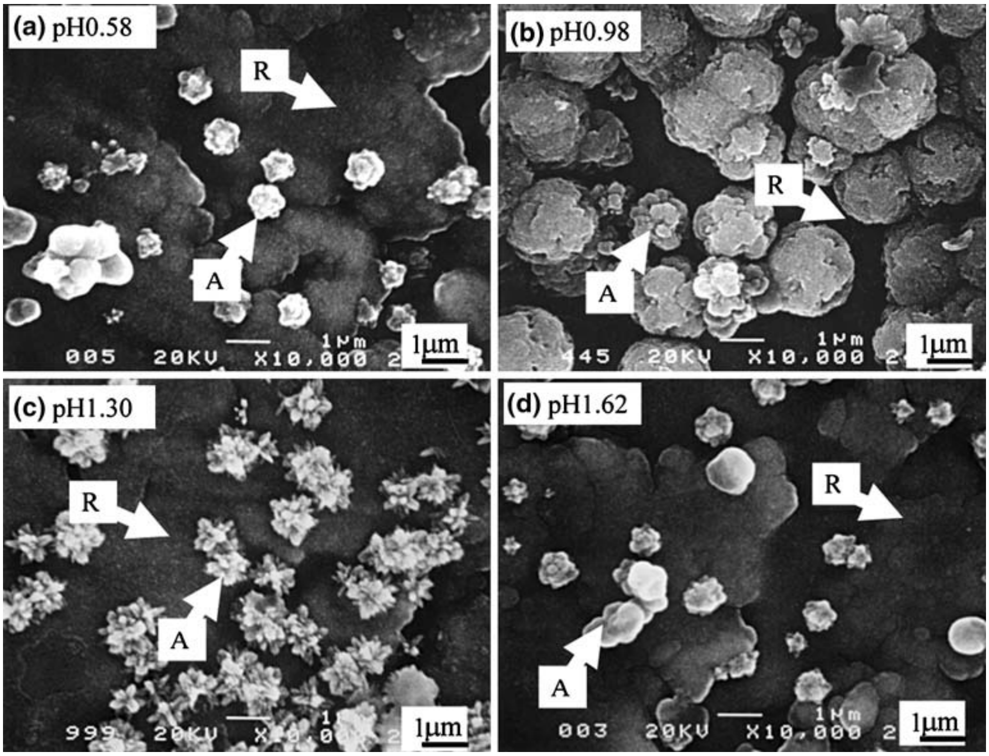

Fig. 3 Surface morphology of the titanium substrates soaked in the treating solution with different pH_i (**a**) 0.58, (**b**) 0.98, (**c**) 1.30 and (**d**) 1.62 at 80 °C for 1 day after ultrasonic rinsing. A: Anatase-rich particles; R: Rutile-rich oxide layer

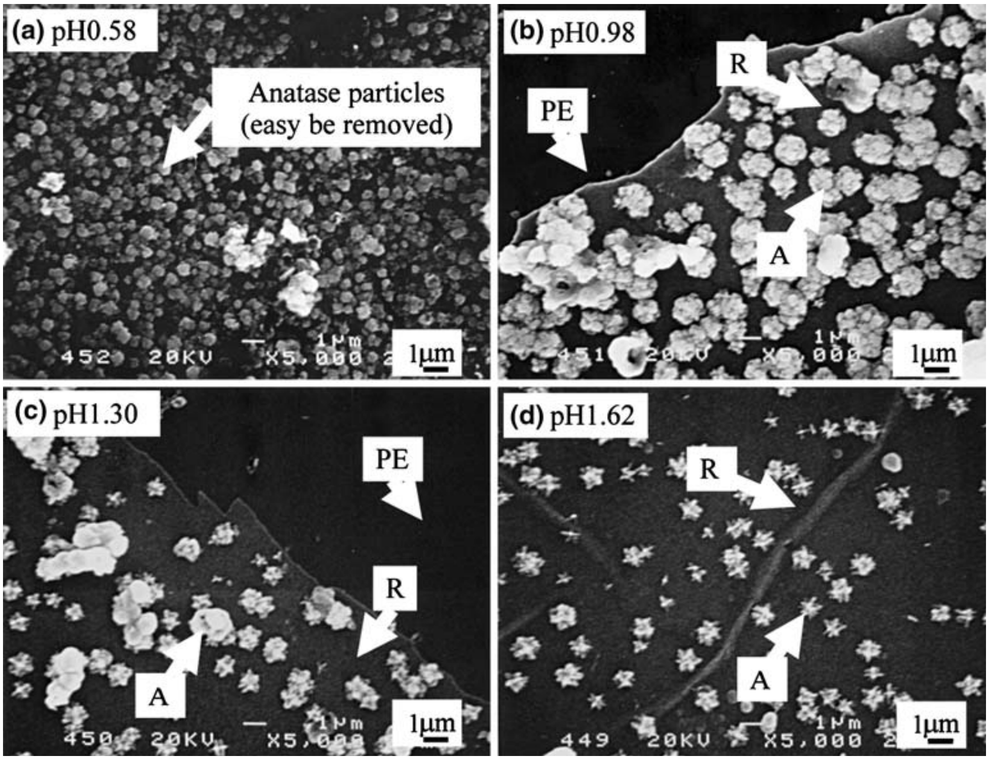

Fig. 4 Surface morphology of the titania layer deposited on PE substrates due to the $TiOSO_4$/H_2O_2 treatment at 80 °C for 1 day with different pH_i: (**a**) 0.58, (**b**) 0.98, (**c**) 1.30 and (**d**) 1.62. A part of the layer was scratched off in (**b**) and (**c**) A: Anatase-rich particles; R: Rutile-rich oxide layer

was scratched off, as in Fig. 4. It is indicted that longer soaking time favors more particles as mentioned before. Within 15 h, the surface layer that consisted of a thin bottom film and bur-like particles (~1 μm in size) scattering on the layer was formed. Here, the bottom film was rutile and the particles were anatase after the XRD profile

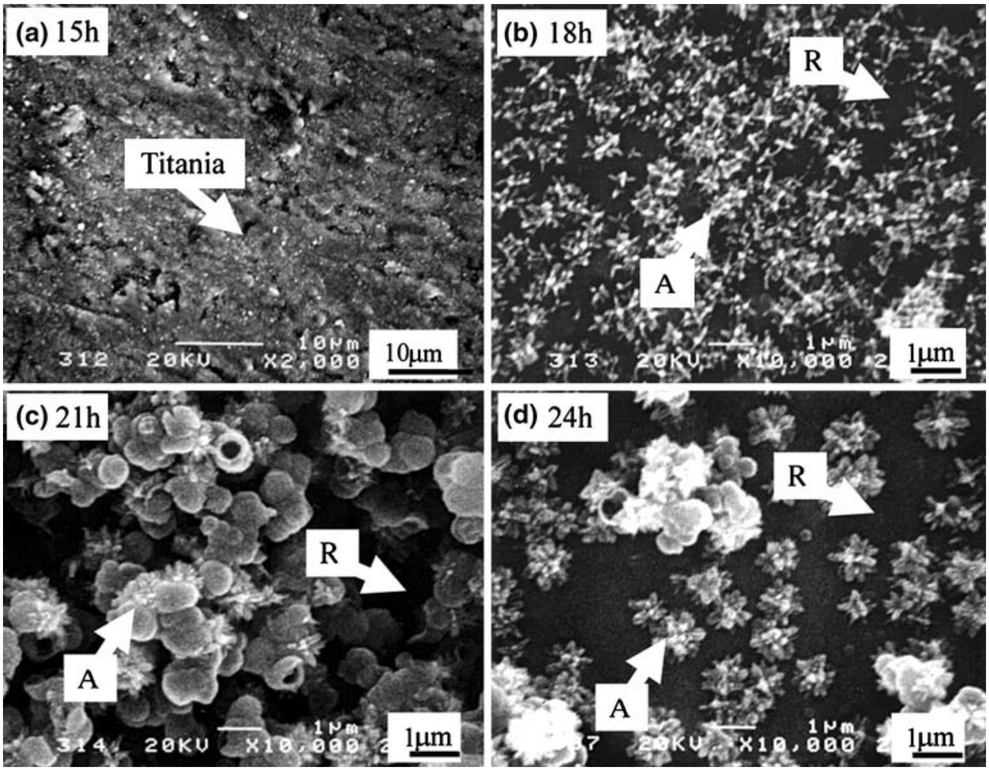

Fig. 5 The effects of the treatment period on surface morphology. The titanium substrates were soaked in the $TiOSO_4/H_2O_2$ solution of pH_i 1.30 at 80 °C for (a) 15 h, (b) 18 h, (c) 21 h and (d) 24 h with ultrasonic rinsing. A: Anatase-rich particles; R: Rutile-rich oxide layer

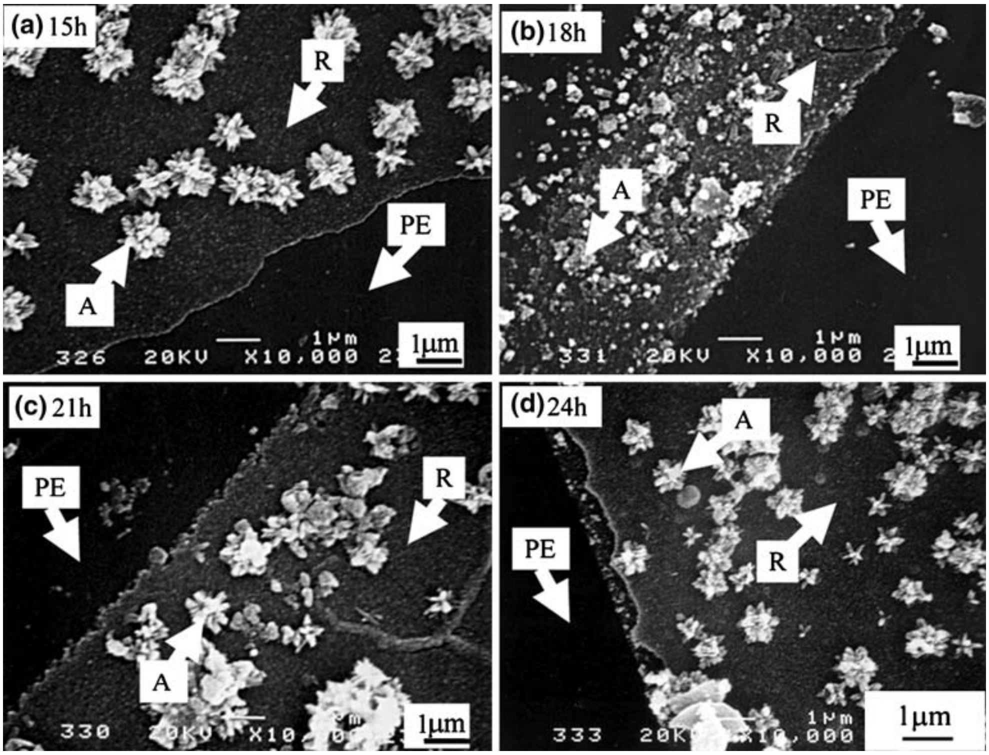

Fig. 6 Surface morphology of Polyethylene substrates soaked in the $TiOSO_4/H_2O_2$ solution of pH_i 1.30 at 80 °C for (**a**) 15 h, (**b**) 18 h, (**c**) 21 h and (**d**) 24 h. A: Anatase-rich particles; R: Rutile-rich oxide layer

change due to the ultrasonic rinsing. With longer treatment, very small particular microstructure appeared in the bottom layer. The size of the upper particles remained constant while their number increased with the treatment period. A little different appearance of the sample for 18 h from that of the others was due to insufficient ultrasonic cleaning.

Apatite deposition in SBF

In order to examine the bioactivity, the titanium samples that were treated with the $TiOSO_4/H_2O_2$ solution (1.3 in pH_i) at 80 °C for up to 24 h and ultrasonically rinsed were soaked in SBF at 36.5 °C for 1 day. Figure 7 indicates their surface morphology, showing many particles, which looked like globular or semi-spherical agglomeration of petal-like crystallites. These particles had the same microstructure as that being characteristic of the apatite particles depositing on bioactive materials [1, 18]. Indeed, their XRD traces (not shown here) confirmed that they were apatite. It is thus evidenced that all of those titania-deposited titanium substrates are in vitro bioactive. Similar apatite deposition was also observed on the PE substrates. Figures 8 and 9 indicate the surface morphology for the PE substrates after they were soaked in SBF at 36.5 °C for 1 day. Apatite particles were found on the titania gel film. Comparing Figs. 7 and 9, the sizes of these apatite particles are the same.

Discussion

The effects of the initial pH value of the treating solutions

In the $TiOSO_4/H_2O_2$ solutions, not only hydrolysis of $TiOSO_4$ but also some other reactions proceed, because the solutions tinted orange. Jere et al. [19] suggested that the formation of a complex $[TiO(H_2O_2)]^{2+}$ was responsible for the tint. Then, Eq. (1) may describe the hydrolysis of $TiOSO_4$.

$$TiOSO_4 + H_2O + H_2O_2 \leftrightarrow TiO_2\ (ppt) + [TiO(H_2O_2))]^{2+} + 2H^+ + (SO_4)^{2-} \tag{1}$$

Thus, both acidity and the complex formation in the solution retard the precipitation of titania, according to the equilibrium equation (1). In contrast, Tengval et al. [20] proposed dissolution of titania under the presence of H_2O_2 to yield some hydrated complexes:

$$Ti(IV)\ (Oxide) + nH_2O \leftrightarrow [Ti(IV)\ (OH)_n^{(4-n)+}] + nH^+ \tag{2}$$

Thus, acidity favors the precipitation of tiania according to Eq. (2), while decomposition of those complexes in either Eq. (1) or (2) leads to titania formation. Another reactions are involved in the titania deposition. Direct corrosive reaction of titanium with hydrogen peroxide might also be taken into consideration for larger H_2O_2 concentrations [8, 15, 17]:

$$Ti + H_2O_2 \rightarrow TiO_2 + H_2\ (aq) \tag{3}$$

Those issues add complexity to the titania deposition reactions. It was also found that the $TiOSO_4/H_2O_2$ solution

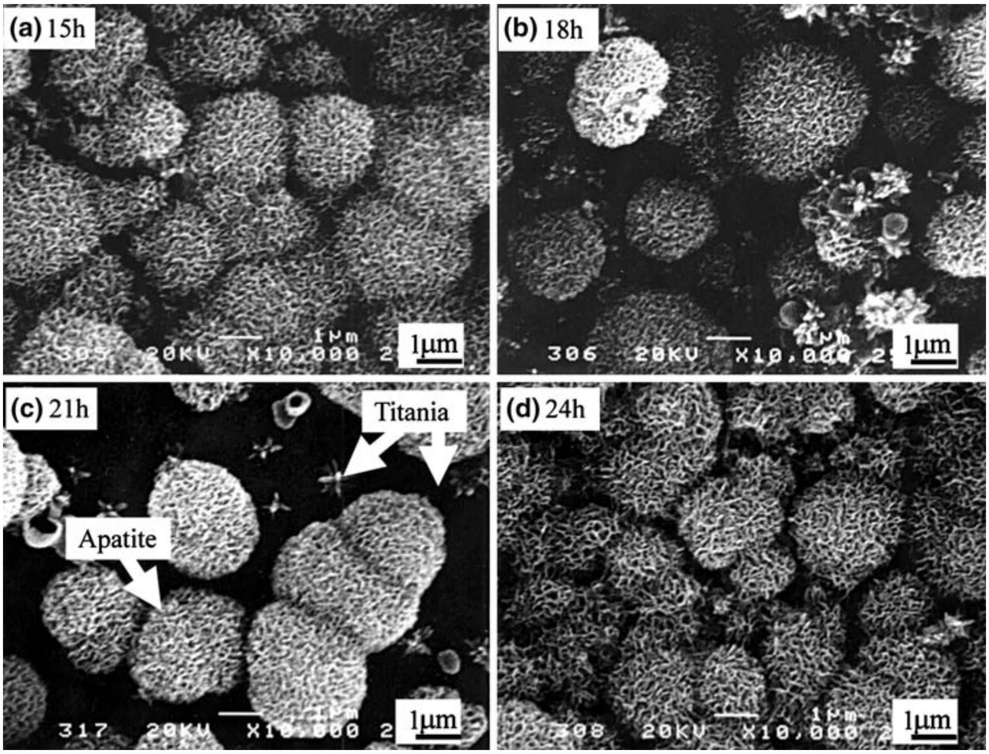

Fig. 7 Apatite deposition on the dual titania layers formed by the $TiOSO_4/H_2O_2$ treatment at 80 °C for (**a**) 15 h, (**b**) 18 h, (**c**) 21 h and (**d**) 24 h with ultrasonic rinsing and subsequently soaked in SBF at 36.5 °C for 1 day

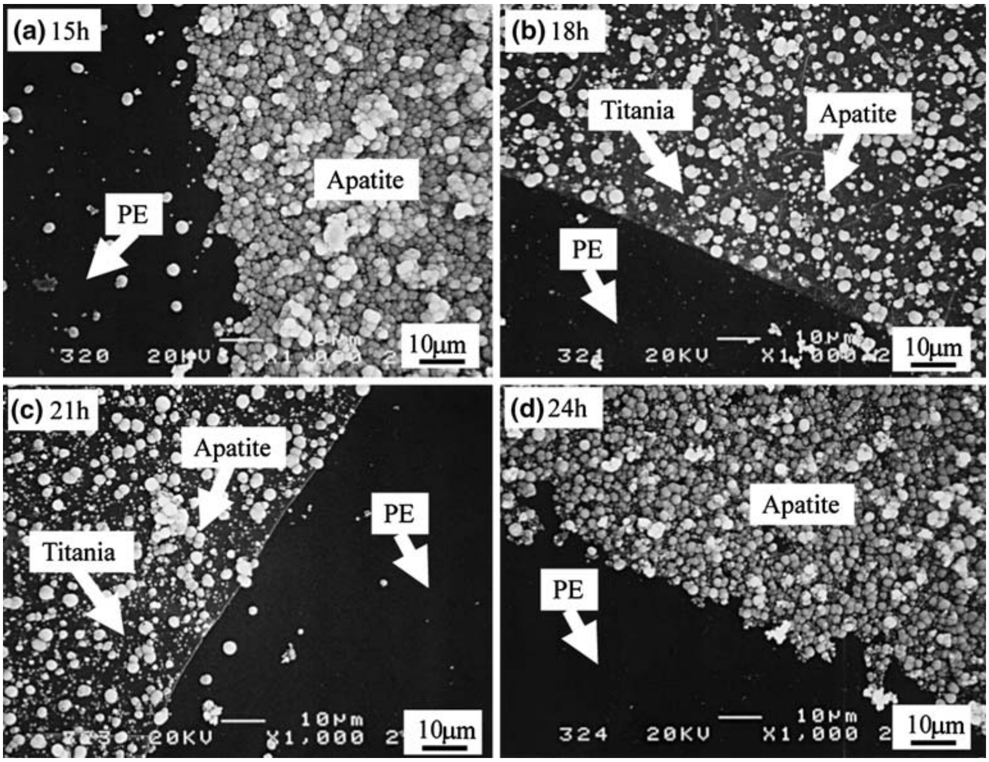

Fig. 8 Surface morphology of polyethylene in $TiOSO_4/H_2O_2$ solution at 80 °C for (**a**) 15 h, (**b**) 18 h, (**c**) 21 h and (**d**) 24 h and subsequently soaked in SBF at 36.5 °C for 1 day

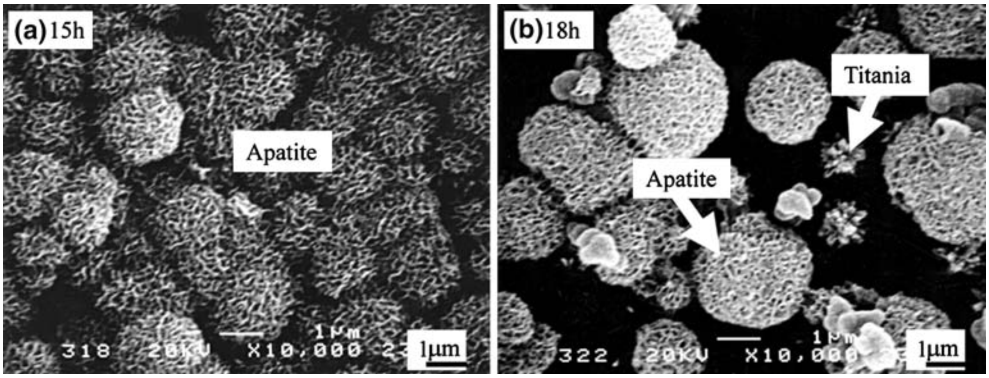

Fig. 9 High magnification of surface morphology on polyethylene in $TiOSO_4/H_2O_2$ solution at 80 °C for (**a**) 15 h and (**b**) 18 h subsequently soaked in SBF at 36.5 °C for 1 day

became free from tint in the later period of reactions in the system involving titanium substrates,. This indicates that the complexes aforementioned in Eqs. (1) and (2) play a key role in precipitation of titania as intermediate species. At this moment, their chemical states and thermochemical stability of Ti(IV) in the solution are unknown, hence, further speculation on counting all equations is meaning less. However, in the framework of eqs. (1) to (3), one may interpret the process of the titania deposition in the following way.

As far as titania deposited on the titanium and PE substrates, one must admit that even at moderate temperatures, employed in the present study (80 °C), the hydrolysis of $TiOSO_4$ is fast enough to deposit thicker titania layers. From the SEM photographs in Figs. 3 and 4 (with scratched area), it is reasonable to conclude that the bottom layers were deposited prior to the precipitation of globular titania. It is confirmed also in our preliminary experiment that the oxidation (Eq. (3)) hardly proceeds under dilute H_2O_2 solutions. Thus, because of the concentration of the present hydrogen peroxide solution as dilute as 0.03 M/l, Eq. (1) is associated with the formation of the bottom layer, though the direct formation of titania according to Eq. (3) cannot be ruled out. Furthermore, the dissolution–deposition equilibrium of Eq. (2) is predominant only after supersaturation in Ti(IV) is achieved and sufficient amount of titania is produced on the substrates. Thus, the reverse reaction of Eq. (2) favors the formation of those agglomerated bur-like or globular particles, consuming the Ti (IV) complexes as the resource derived from the dissolution of as-deposited oxide. The drastic decrease in the anatase peak intensity in TF-XRD patterns (Fig. 1) due to the ultrasonic rinsing is interpreted as showing that the ultrasonic agitation drove off the anatase particles that were loosely bound to the bottom rutile layer. An exception was anatase deposited from the solution with 1.30 in pH_i: Fig. 1 indicated that the apparent X-ray diffraction intensity ratio between anatase and rutile is unchanged after the ultrasonic agitation. Almost constant rutile XRD peak intensity for the PE substrates agreed with the fact that Figs. 4 and 6 indicate the thickness of the bottom layer independent of depositing conditions.

Above discussion is applicable to either substrate. Since no corrosion reaction like that in the titanium substrate was likely to take place between H_2O_2 and PE, the concentration of H_2O_2 was kept higher than that in the case of titanium substrates. As mentioned above, the presence of H_2O_2 in the solution retards the precipitation of titania. That is, the rate of titania deposition on the PE substrates was lower than that on the titanium ones. Therefore, according to Eq. (1), lower pH_i was adequate for depositing titania on PE than on titanium.

The effects of the soaking time in the treating solution at 80 °C

For PE substrates, Eq. (3) is not active. Then, Eq. (1) is first associated with the formation of the bottom rutile layer; meantime, this titania layer was dissolved under the presence of H_2O_2 according to Eq. (2). As time passed, the hydrolysis of $TiOSO_4$ in Eq. (1) caused the acidification of the treating solution, and the deposition of titania in Eq. (2) was related to the formation of those bur-like or globular anatase particles. The dissolution–deposition equilibrium is associated with soaking time. Thus the proper soaking time in the treating solution is also the key point to form the dense titania layer.

Apatite deposition in SBF

Well-crystallized titania was deposited on substrates in the present experiment. These mixed titania layers have apatite-forming ability after being soaked in SBF at 36.5 °C for 1 day. We have observed that the apatite-forming ability of the dense titania layer is obviously enhanced either on the substrates of group (pH) or group (ST). Thus proper pH values and soaking time in treating solution enhance apatite-forming ability or deposition of apatite on the substrates in SBF.

Conclusion

Well-crystallized titania layer consisting of anatase and rutile was deposited on the Ti and PE substrates by soaking them in the 0.03 M $TiOSO_4$ solution at 80 °C for 24 h, and subsequently aged in water at 80 °C for 3 days. They had a dual-layer microstructure: the dense bottom layer and upper porous layer consisting of bur-like or globular particles. The titania deposition is a result of the dissolution–deposition equilibrium associated with pH of the sulfate solution and soaking time. Thus the proper pH value and soaking time in the treating solution are two key points to form the dense titania layer. The resulted titania layers have excellent apatite-forming ability and deposited apatite in SBF within 1d.

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