Research Article

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ZnO-assisted coating of tetracalcium phosphate/gelatin on the polyethylene terephthalate woven nets by atomic layer deposition

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Abstract: A new kind of coating consisting of zinc oxide (ZnO)/tetracalcium phosphate (TTCP)/gelatin (Gel) on the PET woven nets is prepared chemically by the method of atomic layer deposition (ALD) and hydrothermal method. The prepared materials are confirmed by XRD and SEM. XRD results show that ZnO and TTCP are well coated on the surface of PET woven nets and ALD-assisted ZnO leads to a surprising coating adhesion of about 8 MPa. Furthermore, SEM results indicate the diameter and morphology of ZnO, TTCP and Gel of PET woven nets. And the water contact angles of PET's surface are decreased with ZnO, TTCP and Gel of PET woven nets. Moreover, the confocal imaging of NIH3T3 cells shows that the obtained product could promote the cells proliferation, which indicates that the good biocompatibility of the prepared PET/ZnO/TTCP/Gel woven builds a foundation for their future application. The results aim to obtain an efficient method to modify PET for fabricating an ideal artificial implant meeting the clinical needs, and imply a positive effect in promoting the compatibility of PET for enhancing graft-bone healing after implantation.

Keywords: atomic layer deposition; PET woven nets; zinc oxide; tetracalcium phosphate; gelatin

1 Introduction

Polyethylene terephthalate (PET) material has been applied to the biomedical devices for its excellent mechanical strength, including artificial ligament, artificial vessel, heart valve closure, surgical suture and so on (1). However, it is difficult for cells to adhere and proliferate on PET fibers due to a low surface energy of PET. Thus, to overcome the disadvantages of PET biological inertness and improve the interaction between PET and host tissues, scientists have widely studied on the surface modification of PET material (2-6). Many bioactive materials or hydrophilic polymers have been used for the coating of PET materials for their medical and biomedical applications such as surgical drapes, vascular grafts and ligament prostheses (7-10). Nevertheless, although some surface modifications based on different chemical reactions have been reported, it is difficult to carry out the surface modification on PET material with a high coating adhesion due to the chemical inertia, high crystallinity and hydrophobic specialties of PET.

Atomic layer deposition (ALD) is a surface-controlled layer-by-layer process that results in the deposition of thin films one atomic layer at a time. The self-limited character of ALD ensures the growth of uniform and conformal films, with film thickness controlled at the atomic level (11). Until now, many materials have been obtained through ALD technology (12). In addition, atomic level control and low deposition temperature allow for a precise coating on biological templates, including TiO_2 and Al_2O_3 on tobacco Mosaic virus, fungus hair, ferritin, etc. (13,14). Furthermore, compared with other nanostructure fabrication techniques, ALD on the biological template can accurately control monodisperse

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functional units determined by the information encoded in DNA. Moreover, the obtained ALD films with different crystal structures can be obtained by adjusting the substrate temperature (15), which provides a potential opportunity for the growth of other materials based on crystal surface matching (16). Therefore, based on the above previous reports, ALD would be a good substitute for PET surface modification.

Calcium phosphate ceramics is one of important biomedical bioactive ceramic materials, which composed of HA ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), TTCP ($\text{Ca}_4(\text{PO}_4)_2\text{O}$), α -TCP ($\text{Ca}_3(\text{PO}_4)_2$), β -TCP ($\text{Ca}_3(\text{PO}_4)_2$), and so on. These calcium phosphate ceramics are always used as a surface modifier for bioactive coating on hard or soft material, including titanium alloy, stainless steel, PET, polyetheretherketone (PEEK), and so on, from some strategies of plasma spray, sol-gel, electrochemical deposition, etc. In the present experiment, we develops a novel surface modification based on our research results of the preparation about a nanoscale surface roughness ZnO film by ALD technology changes their matrix adhesion (17-18), which means that the deposition of ZnO with ALD technique is used to obtain a coating on PET woven nets. Furthermore, the combination of the advantages of TTCP and gelatin gives a good choice for the artificial bioactive coatings. Therefore, a novel PET/ZnO/TTCP/Gel woven net is prepared, which shows a good adhesion between the coating and PET woven nets of about 8 MPa. To be specific, the current study is carried out in terms of two folds: (1) to obtain an efficient method to modify PET for fabricating an ideal artificial implant meeting the clinical needs, (2) to imply a positive effect in promoting the compatibility of PET for enhancing graft-bone healing after implantation.

2 Experimental

2.1 Pretreatment of PET woven nets

The PET woven nets were immersed in an ethanol solution for 0.5 h and then treated by sonication to remove surface adhesive impurities. After being washed with distilled water to remove the residual ethanol at room temperature, PET woven nets were further boiled in 1% sodium hydroxide solution for 1 h. Then, the obtained PET was washed with plenty of distilled water until the pH value of the wash solution was near neutral. Finally, the carboxyl exposed PET woven nets were obtained after being dried at 60°C (19).

2.2 ZnO deposition on PET woven nets

ZnO was deposited on PET woven nets using Picosum R-150 ALD UNIT. Diethylzinc (DEZ, purity > 99.99%) was used as Zn precursor, and water was used as O precursor. The two precursors were pulsed into the reaction chamber alternately with a high nitrogen (purity > 99.999%) as carrier gas. A complete ALD cycle consists of two precursor pulses and two purge processes. The pulse time of precursors was 0.1 s, and the puege times for DEZ and water 3 and 4 s, respectively. During deposition, the pressure of chamber was kept about 1400 Pa by an oil pump, and the substrate temperature was set to 150°C. The number of ALD cycles was fixed at 300, and the obtained product was recorded by PET/ZnO woven nets.

2.3 Hydrothermal synthesis of TTCP on PET/ZnO woven nets

1 mol/L calcium nitrate solution and 0.6 mol/L orthophosphoric acid solution were put into a three-necked bottle with the Ca/P ratio of 2:1. Then, urea was put into the above solution as the mass ratio of 5%. After being stirred for several minutes, 25% ammonia solution was added to adjust pH to 10 at 40°C for 4 h. The obtained solution and PET woven nets were transferred to polytetrafluoroethylene lined autoclave and then kept for 6 h at 90°C. Finally, PET/ZnO/TTCP woven nets were produced after washed by distilled water and dried 60°C for 12 h.

2.4 Adsorption of Gel on PET/ZnO/TTCP woven nets

The prepared PET/ZnO/TTCP PET woven nets were immersed in the Gel solution at different content of 1%, 5% and 10% (w/w) for 24 h. The obtained woven nets were kept at drying oven at 60°C for 24 h after being washed by deionized water, whose product was recorded as PET/ZnO/TTCP/Gel woven nets.

2.5 Characterization

The thickness of ALD ZnO on the Si wafer under the same deposition situation to the ZnO deposition on PET woven nets was measured by ellipsometer (W-VASE with AutoRetarder, J.A. Woollam CO., Inc. USA), and then the deposition rate was calculated. The phase and purity of the obtained product was determined by powder X-ray

diffraction (XRD) (RigakuD/MAXIIA diffractometer using Cu K α radiation). Energy dispersive X-ray (EDX) analysis was recorded on field-emission scanning electron microscope (FESEM, Hitachi, S-4800). The coating adhesion was performed according to ASTM D751-2005 by an electronic universal testing machine (CXT-4104, MTS Systems Corporation, Eden Prairie, MN, USA). Surface wettability was characterized by static water contact angle measurement (JC2000C1, Zhongchen Co., Ltd.).

2.6 Confocal imaging of cells

Confocal imaging of cells was performed using a Leica laser scanning confocal microscope (Wetzlar, Germany). NIH3T3 cells (1×10^6 cells·mL⁻¹) were incubated with PET/ZnO/TTCP/Gel woven nets for 2 h for confocal imaging, fixed with 4% paraformaldehyde for 30 min, and stained by DAPI for 8 min. All cells were washed twice with PBS before confocal imaging from 1 to 6 days of culturing time. Imaging of NIH3T3 cells was carried out at the laser excitation of 364 nm, with the maximum emission peak is 454 nm.

3 Results and discussion

The ZnO/TTCP/Gel coated PET woven nets are prepared by the following three-step procedure: After the carboxyl group exposure of the PET woven nets, ZnO, TTCP and Gel was deposited on PET woven nets, orderly. Among them, ZnO is deposited by ALD technology and TTCP was grown by hydrothermal synthesis, in which ZnO deposition is a key step for the strong coating adhesion between PET woven nets and coating. Thus, as shown in Figure 1, the PET woven net is first treated with NaOH to expose the carboxyl groups to the surface (19), which can greatly alter the activation and hydrophobicity of the PET woven nets. Furthermore, ZnO is coated on a clean PET woven net by placing ZnO in an atomic layer deposition instrument, which can cover a ZnO film with nanometers on the surface of PET woven nets with a deposition rate of 0.13 nm/cycle. Then, the above PET nets are immersed in calcium and phosphate salt solution to hydrothermally grow TTCP because of a possible crystal face matching between TTCP and ZnO (15,16).

EDS and XRD analyses were performed to identify the chemical component and crystalline nature of the deposit surface. EDS analyse shows 1.01, 0.54 and 2.27 mol% about Ca, P and Na element, respectively, meaning an average Ca/P ratio of 1.87. The result is different from the Ca/P ratio of normal HA (1.67), which

implies a possible newly formed surface-deposit as matching the Ca/P ratio (20,21). Moreover, the desired Zn element with 0.06 mol% is found in the final product of PET/ZnO/TTCP woven nets, but the atomic percentages of Zn element is 5.72 mol% in the intermediate product of PET/ZnO woven nets, which confirms the presence of ZnO. Furthermore, Figure 2 shows the typical XRD pattern of the obtained products. As shown in curve a, the reflection peaks labeled by circle can be indexed to the main lattice plane of PET, but the other reflection peaks marked by circle asterisk can contribute to the

Figure 1: The procedure of the preparation of the ZnO/TTCP coated PET woven nets.

Figure 2: The XRD patterns of PET/ZnO and PET/ZnO/TTCP woven nets.

main peak of ZnO (JCPDS 80-0074). Closer observation shows that (002) and (001) crystals appear, but the normal strongest peak of (101) crystal face is invisible, which indicates a poor crystallization of ZnO amorphous structure and meanwhile implies a thin ZnO film about few nanosize in thickness on the surface of PET woven nets. The result implies that ZnO can be coated on the surface of PET woven nets successfully for the formation of PET/ZnO woven nets. Furthermore, calcium phosphate is characterized after the hydrothermal treatment of PET/ZnO woven nets. As shown in curve b, beside the typical PET diffraction peaks, the peaks of ZnO phases disappear and the present of the major peaks of TTCP phases is located at respectively 25.4° , 29.1° , 30.6° and 32.4° (JCPDS 70-1379). The result is obvious different from the previous many reports on calcium phosphate coating by the matter of HA and TCP. Closer observation shows that the peak widening seems to occur as indicated by the enlargement of the peak at 25.4° and 32.4° and the absence of ZnO phases could contribute to a thick cover, which proves that the diffracting amorphous matter significantly obtains in importance on the surface of PET woven nets with a ZnO transition layer. The results show amorphous ZnO obtained by ALD technology helps to modify PET by amorphous TTCP. Therefore, it is feasible of the preparation of TTCP modified woven nets through ZnO deposition by ALD technology and further TTCP growth by hydrothermal treatment.

The morphology of PET, PET/ZnO and PET/ZnO/TTCP woven net is characterized by SEM. As shown in Figure 3, the average diameter of the PET woven nets is about $20 \pm 1.3 \mu\text{m}$, and their surface looks smooth after being treated by NaOH (Figure 3a). However, the surfaces are slightly rough and the average diameter is increased to about $22 \pm 1.8 \mu\text{m}$ by ZnO deposition by ALD technique (Figure 3b). A closer look reveals that the deposition is coated on the surface of PET woven nets (Figure 3c). A partially magnified SEM image (marked with a circle in Figure 3c) indicates that many nanoparticles are well-dispersed with approximately 20 nm in uniform sizes (Figure 3d). The results imply that the PET woven nets are covered with ZnO deposition in nanometer sizes. Furthermore, TTCP is grown by hydrothermal synthesis followed by an ALD process. As shown in Figure 3e, their surfaces became rough and the average diameter is further increased to about $27 \pm 2.1 \mu\text{m}$, which could attribute to the coverage of a large amount of irregular TTCP. The cracked portion marked with a circle in Figure 3e shows a thick coating of TTCP modification, which can be attributed to a significant broadening of the fiber diameter. In addition, the enlarged SEM image

shows a large amount of irregular coverage on the surface of the woven net (Figure 3f). These results indicate that TTCP can be strongly modified on PET woven nets with the assistance of ZnO nanoparticles produced by ALD technology.

Due to its potential biomedical applications in the body, Gel is further coated on the PET/ZnO/TTCP woven nets to obtain good biological activity. The PET/ZnO/TTCP woven nets were immersed in 1, 5 and 10% (w/w) Gel aqueous solution, which is characterized by SEM. As shown in Figure 4, as the content of Gel increases, the average diameter increases from $27 \pm 2.1 \mu\text{m}$ to $30 \pm 3.2 \mu\text{m}$ (Figures 4a, 4c and 4e), and the fibers of the PET woven nets look smoother and smoother (Figures 4b, 4d and 4f). The results imply that the PET/ZnO/TTCP woven nets are covered with a large amount of organic matter. Thus, compared to the images of Figures 4a and 4b, it is plane for the fibers of the PET woven nets in Figures 4c-f, which contributes to the presence of poorly conductive Gel. Therefore, a ZnO/TTCP/Gel composite coating on PET woven nets is successfully prepared in this experiment. According to the previous reports (22,23), the hydrophilic property of polymer surface always can be evaluated by the water contact angle. As shown in Figure 5, the contact angle decreased from 92° to 42° after the application of different coating. Specially, PET's surface water contact

Figure 3: SEM images of PET (a), PET/ZnO (b-d) and PET/ZnO/TTCP (e,f) woven nets.

angle with treatment by NaOH is 92° (Figure 5a), which is low than a net PET (24), indicating that the original PET surface is hydrophilic. After ZnO deposition by ALD and TTCP coating by hydrothermal synthesis, the water contact angles decrease to 78° and 65° (Figures 5b and 5c), respectively, indicating that the hydrophilicity of the PET surface increases along with further material's

modification, which can attribute to hydrophilic materials and porous structure. Furthermore, Gel contributes to a more hydrophilic surface, which results from a water contact angle of 42° (Figure 5d).

The adhesion of ZnO/TTCP/Gel coating on PET woven nets is evaluated according to ASTM D751-2005, the Standard Test Methods for Coated Fabrics. Based on our homemade jig (Figure 6a), the coating adhesion is about 8 MPa (Figure 6b), which may result from a composite chemical reactions of ZnO deposition on surface on PET woven nets by ALD technology compactly and then TTCP growth on ZnO surface through a hydrothermal synthesis.

It is necessary to assess the bioactive characteristics of PET/ZnO/TTCP/Gel woven nets, because they could be potentially used in biomedical applications. Figure 7 shows the CLSM photographs of NIH3T3 cells incubated on the woven nets for 1, 2, 3, 4, 5 and 6 days. When the cells were grown on the PET/ZnO/TTCP/Gel woven nets, the number of cells is increased over time, indicating that the cells proliferated well with increasing days. The results imply that the PET/ZnO/TTCP/Gel woven nets have good

Figure 4: SEM of the PET/ZnO/TTCP/Gel woven nets with different Gel content: 1% (a,b), 5% (c,d) and 10% (e,f).

Figure 5: Water contact angle image of carboxyl exposed PET (a), PET/ZnO (b), PET/ZnO/TTCP (c) and PET/ZnO/TTCP/Gel (d) woven nets.

Figure 6: The jig photo (a) and the curve (b) of the coating adhesion between ZnO/TTCP/Gel coating and PET woven nets.

Figure 7: The fluorescent images of cells incubated on the PET/ZnO/TTCP/Gel woven nets for 1 day (a1,b1,c1), 2 day (a2,b2,c2), 3 day (a3,b3,c3), 4 day (a4,b4,c4), 5 day (a5,b5,c5) and 6 day (a6,b6,c6) under the identical instrumental conditions at 100× magnification and are presented at the same intensity scale.

biocompatibility and biological activity, which lays a good foundation for future applications.

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4 Conclusion

The PET/ZnO/TTCP/Gel woven nets are prepared by ALD and hydrothermal method, and a strong coating adhesion between ZnO/TTCP/Gel coating and PET woven nets is about 8 MPa. The reason can contribute to the chemical growth of ZnO by ALD technology and TTCP by hydrothermal synthesis. The results show that ZnO nanoparticles can cover on the surface of the PET woven nets, which is used as a medium for further TTCP growth. With ZnO deposition and TTCP growth, the average diameter increased from $22 \pm 1.8 \mu\text{m}$ to $27 \pm 2.1 \mu\text{m}$, and the surface of the PET woven nets became very rough. Moreover, with the addition of Gel, the average diameter is further increased to $30 \pm 3.2 \mu\text{m}$, but the surface of the PET woven nets looks smoother because a large amount of Gel can be applied on the PET/ZnO/TTCP woven nets. Additionally, the cell experiments reveal that the PET/ZnO/TTCP/Gel woven nets have good biocompatibility and biological activity, which lays a good foundation for its future application.

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