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Singlet oxygen generating nanolayer coatings on NiTi alloy for photodynamic application

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ABSTRACT

Photodynamic Therapy (PDT) is a promising approach for killing microorganism and especially for the inactivation of antibiotic-resistant strains. The photodynamic process rapidly generates reactive oxygen species (ROS) as for instance peroxides, hydroxyl radicals, superoxide ions, and singlet oxygen. Among them, the singlet oxygen is considered to be a major causative agent of cellular damage in photodynamic process. Due to advantage of the cytotoxic effect of PDT on bacteria, the PDT method has been one of the most appropriate tools to prevent the microbes which result in biofilm formation. This work describes a method of singlet oxygen generating nanolayer coating on NiTi alloy which shows a good biocompatibility. The 5,10,15-triphenyl-20-(4-carboxyphenyl)-porphyrin] platinum (PtCP) functional nanolayer coatings were prepared in two steps. In the first step, Al coating was prepared on biomedical NiTi alloy substrate by DC magnetron sputtering, and then this coated substrate alloy was immersed into hot water to form Al_2O_3 coatings. In the second step, a photosensitizer (PS) with carboxyl group was chemically attached to the hydroxyl-terminated Al_2O_3 coatings by a direct esterification method. The microstructure and the elemental and phase composition of the coating were investigated by scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDS), and X-ray diffraction (XRD). Results from this study show that the PtCP functional nanolayer coating is composed of many perpendicular nanosheet structures. These very thin nanosheet structures with the thickness of a few nanometers mainly show amorphous phase. The singlet oxygen generation efficiency of the PS being chemically bonded on these nanosheets was detected by an indirect chemical method by using the decomposition of 1,3-diphenyl-isobenzofuran (DPBF).

1. Introduction

Over the last decade, PDT has been used to be a light-activated new modality to treat diseases ranging from cancer to antibiotic-resistant infections [1–4]. PDT combines a nontoxic PS and harmless visible light to produce reactive oxygen species that can kill mammalian and microbial cells. During PDT, the delivery of visible light at the appropriate wavelength is necessary to excite the PS molecule to higher excited singlet state. This excited state may then undergo intersystem crossing to the slightly lower energy, but longer-lived triplet state. This triplet state of the PS can either interact with oxygen to produce singlet oxygen (Type II reaction) or directly react with the molecules near the immediate vicinity (Type I reaction) [5–10]. Although the bacterial killing can be mediated by either of the above mentioned reactions, it is known that the singlet oxygen is the predominant chemical entity causing cell death. Recently, a series of researches have shown that it is possible to kill bacteria by using ROS that is generated from photosensitizers such as methylene blue (MB) or toluidine blue O (TBO) [11–14]. In addition, bacteria, as well as fungi, yeasts, and viruses, treated with photosensitizers were shown to be successfully killed by visible light [15].

NiTi alloy has been one of the most popular metallic implant materials due to its unique properties such as shape memory effect, superelastic properties, good biocompatibility, cytotoxicity and high corrosion resistance [16,17]. These novel properties enable it to be widely used in industrial applications as well as medical and dental applications [18]. Therefore, technology of PDT agent coatings on biocompatible material is becoming a very important because these functional materials can prevent the microbes which result in biofilm formation and infections.

In the present study, we have come up with a new method to fabricate the singlet oxygen generating nanolayer coatings on

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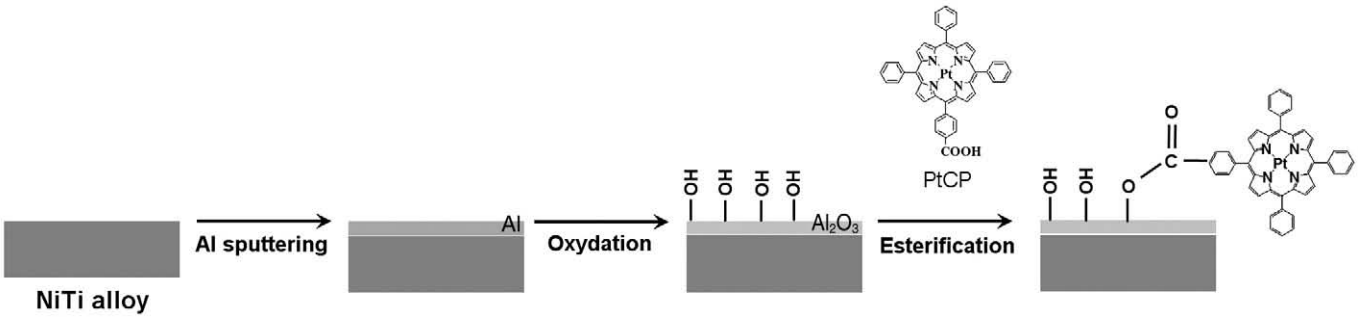

Scheme 1. Fabrication procedure of singlet oxygen generating nanolayer coatings on NiTi alloy.

biomedical NiTi alloy. First, Al_2O_3 coating was deposited on NiTi alloy substrate by DC magnetron sputtering and oxidation process. And then the PtCP molecules with carboxyl group were chemically attached to the hydroxyl-terminated Al_2O_3 coatings by a direct esterification method.

2. Experimental

2.1. Preparation of the PtCP functional nanolayer coatings

A commercial NiTi alloy (Beijing Gee SMA Technology Co. Ltd, China) with the composition of Ni–51.83Ti–48.17 at.% was cut into samples of 9 mm in diameter and 0.2 mm thickness for the substrate material. The surface was cleaned ultrasonically in acetone and distilled water and then dried at 90 °C. Al coating was deposited on NiTi alloy substrate by DC magnetron sputtering by using the metallic aluminum (99.99%) target. The distance between the target and the substrate was 10 cm. The vacuum chamber was pumped down to the pressure of 1.0×10^{-5} Pa. During the coating deposition, flow of Ar gas was kept constantly at 30 sccm. The direct current (DC) sputtering power applied on the target was maintained at 300 W and the substrate temperature was at room temperature. To oxidize the Al coatings, the Al sputtered NiTi alloy was immersed into hot water at 90 °C for 90 min. After washing and drying, Al_2O_3 coated NiTi alloy was immersed in 10 mL of 2.0×10^{-5} M PtCP/toluene solution and introduced into a shaking water bath. The speed and temperature of the shaker water bath were maintained at 100 rpm and 40 °C, respectively, for 24 h. After 24 h, Al_2O_3 coated NiTi alloy was cleaned using toluene and distilled water. PtCP was synthesized as previously described [19].

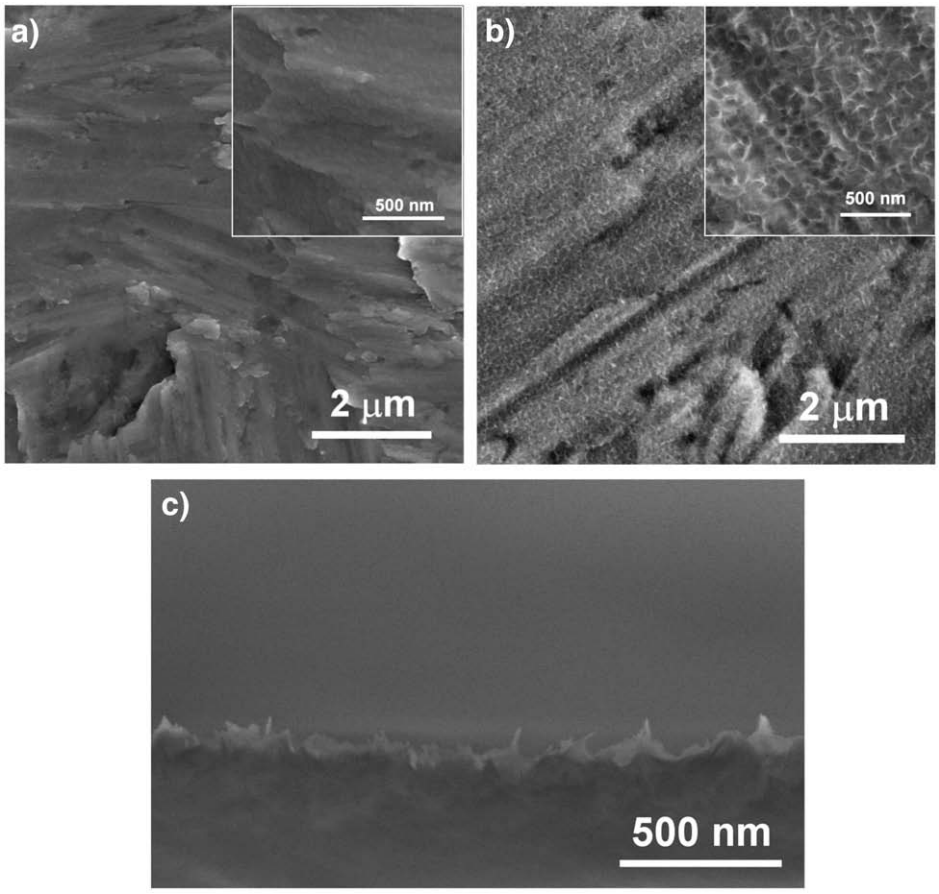

Fig. 1. FE-SEM images of the surface and cross-sectional morphologies of (a) Al coating before oxidation reaction and (b,c) after oxidation reaction of Al coatings at 90 °C for 90 min. The inset represents the high magnification image.