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Platelet Adhesion onto Nitinol Surfaces Modified by Microwave Cold-plasma

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Abstract: The macromolecular structures on nitinol surfaces were prepared by ECR microwave cold-plasma of tetraglyme conditions. The surface chemistry was characterized by high resolution ESCA. The results showed that the modified nitinol surfaces were built up mainly of $-CH_2-CH_2-O-$ linkages and were particularly effective in preventing platelet adhesion.

Keywords: Nitinol, cold-plasma modification, platelet adhesion.

The combination of shape memory effect and superelasticity with good biocompatibility makes nitinol especially suitable for medical applications[1]. The wide spectrum of application imposes special requirements on the biocompatibility of nitinol. Bio-fouling is another important measure of biocompatibility because of the strong affinity for physical adsorption of proteins to nitinol surfaces[2]. More importantly, the adsorbed protein layer can further mediate additional biological responses. Non specific protein adsorption and cell attachments are surface reactions, surface modification of nitinol is one approach to control bio-fouling[3]. A promising approach is based on poly (ethylene glycol), or PEG. PEG is a neutral, hydrophilic hydrogel that effectively forms hydrogen bonds with water. The structured water layer is thought to contribute to the protein resistance of PEG[4]. Here we present a surface coating technique of tetraglyme [CH_3-O-(CH_2-CH_2-O)$_4$-CH_3] cold-plasma deposition to achieve modified nitinol surfaces, which is expected to show new functions of nitinol to enhance its biocompatibility in protein resistance.

The apparatus for preparation of PEG-like coatings on nitinol used in this study is an electron cyclotron resonance (ECR) microwave cold-plasma system, with the frequency 2.45 GHz, power 130 KW in 1.5 ms pulse[5]. All plasma treatment was preceded by evacuation and purging of nitinol, vapor, and gas supply lines, and oxygen-exposure of the reaction chamber to a 30 min oxygen-plasma environment, tetraglyme vapor was introduced to the chamber at a flow rate 1.3 mL/s. The plasma power was first maintained at 80 W for 2 minutes at 350 mT, then reduced to deposit the

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functional PEG-like coating. It was maintained at 15 W for one minute, then at 10 W for another one minute for a total plasma-on time of 4 minutes. Plasma treatments were performed at a reactor temperature of 25°C.

The ESCA measurements of samples were performed at 25°C with a XSAM800 KRATOS instrument system employing monochromatic Mg Ka radiation at 300 W and 20 mA. A take-off angle was 55° and a binding energy range in 0-1000 eV (a pass energy of 89.45 eV at 1 eV/step) used in all sample analysis. Platelet-rich plasma (PRP) having a 2.43×10^5 cell μL^{-1} concentration was obtained (Wuhan Tianhui Bioengineering Co., Ltd.). Nitinol samples were hydrated in phosphate-buffered saline (PBS; pH 7.4). Each rehydrated film was transferred into a PRP prewarmed to 37°C, the samples were washed carefully with PBS to remove weakly adhered platelets. Platelets adherent on the nitnol surfaces were fixed with a 2.5% glutaraldehyde in PBS for 10 min at 25°C and then dehydrated in an ethanolgrade series for 10 min after each was washed with PBS, and dried on a clean hood at 25°C. The platelet attached to the nitnol surfaces modified by tetraglyme cold-plasma was investigated by a scanning electron microscope (SEM; JSM-840A, JEOL Co., Japan) with a tilt angle of 45°.

Figure 1 shows the carbon 1S high-resolution scan of modified nitinol. The dominant carbon functional group is the ether (C-O) group at 286.3 eV. There is a small peak at 288.9 eV from the C-C crosslinks, and another peak at 290.8 eV and 290.6 eV from the higher oxidized carbons. The macromolecular layers contained significant amounts of C=O, O-C=O, and O-CO-O functionalities. It is concluded that the coating retained its PEG-like characteristics after the plasma modification process. These findings support our initial hypothesis that the formation of oxygen-plasma-generated structures and active species *(e.g.,* free-radical sites) rendered a surface recombination mechanism of tri(ethylene glycol) dimethyl-ether origin molecular fragments different from that developed on a nonoxidized surface. It also should be noted that free-radical species trapped in the nascent macromolecular networks could initiate intense *ex situ* oxidation reactions under open laboratory conditions.

Figure 1 ESCA carbon 1S high-resolution scan spectrum of nitinol from plasma modification

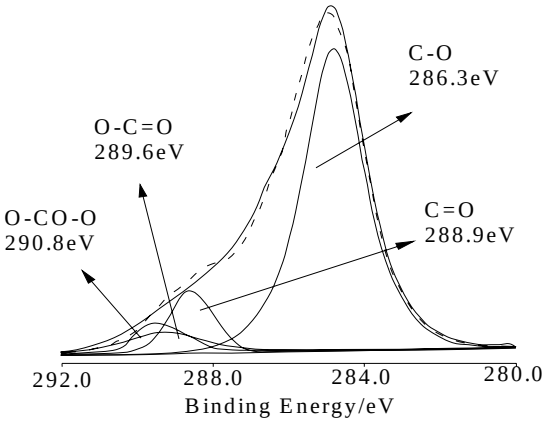
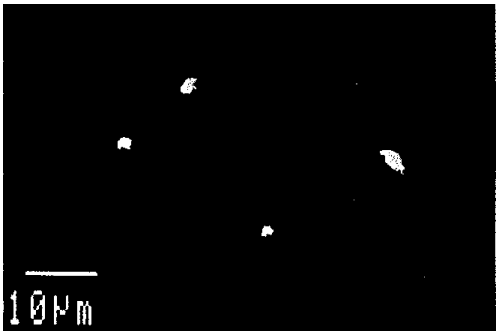


Figure 2 shows the SEM picture of platelets attached to the modified nitinol surfaces. It was observed that the platelet adhesion on the modified nitinal significantly decreased. We can see that a nitinol surface by tetraglyme plasma modified has biocompatible properties and it was particularly effective for the prevention of platelet adhesion. Possible explanation for protein resistance of PEG-like structures on nitinol was provided including its low interfacial free energy, hydrophilicity, high surface mobility, and steric stabilization effect.

Figure 2 SEM photographs of platelet adhesion to nitinol after tetraglyme plasma modification



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