Effect of gold deposition onto titanium on the adsorption of alkanethiols as the protein linker functionalizing the metal surface

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A new method to enhance the biofunctionalization of Ti materials was developed by the immersion of Au-sputtered titanium plates into a solution of alkanethiol with a carboxy group end (HS-C11-COOH). X-ray photoelectron spectroscopy (XPS) analysis showed that the gold content increased with the Au sputtering time and reached over 98 at% after 100 s. The content of the characteristic alkanethiol elements (S, C, and O) in the immersed Ti specimens increased with the Au sputtering time, which indicates that the binding of alkanethiol molecules is enhanced by the Au modification on the Ti surface. Qualitative analysis of XPS (Au-S, COO−, and OH− species) and FTIR spectra (peaks assignable to an aliphatic carboxylic acid) for the sample after immersion also supported this. A strong positive correlation between the S and Au content confirms that Au sputtering is an effective method to control the alkanethiol treatment of Ti substrates.

Keywords: Au deposition, Titanium substrate, Alkanethiol, XPS, FTIR

INTRODUCTION

The use of metallic materials for medical devices that directly contact biological tissue requires biofunctions such as osteoconductivity, antithrombotic properties and biocompatibility, depending on the purpose. Thus, surface treatment (modification) of the device and selection of the metal species becomes necessary. While titanium (Ti) and its alloys are highly biocompatible (bioinert) materials with excellent mechanical properties, additional surface modification is necessary to achieve higher biofunctionality, such as specific cell attachment ability. This can often be realized using methods such as silanization1−6, tressyl chloride activation7, sol/gel8, plasma spray9,10, and electrodeposition11.

While Ti implants have recently become the most common choice for dental implant treatment, they have an essential drawback as a natural dental root replacement in that they lack periodontal membrane functions such as sensing and absorption of externally applied forces or the protection of the periodontal tissue from infection by epithelial attachment. Thus, a Ti implant body with an artificial periodontal membrane is more desirable. To realize this, it is necessary to modify the Ti implant surface mechanically, physically or chemically, so that the periodontal membrane cells can easily attach, accumulate, and differentiate on the implant surface. Among the various methods, the chemical approach may be the most promising, where adhesive peptides, to which the cells anchor, are firmly attached onto the metal.

Besides direct treasylation of the Ti surface7, there are several methods to increase the affinity of Ti toward periodontal membrane cells. For example, Matsumura et al. introduced carboxy groups onto the Ti surface by two steps; the Ti surface was first coated with an ethylene-vinyl alcohol copolymer, which was then oxidized with ozone to form carboxy groups12. While this may be a simple way to introduce functional groups onto the Ti surface, it is difficult to determine the type and amount of hydrophilic functional groups that result with this method.

Another method also consists of two steps where gold is first deposited on the Ti surface and then certain functional “linker” molecules with thiol endgroups are firmly attached onto the modified surface by S-Au bonds. The advantage of this linker approach is that the surface properties may be widely varied according to the type of functional group in the linker molecule. The introduced functional groups can be further modified with appropriate peptide motifs aimed at specific cell attachment. Among the various types of functional groups, carboxy or amino groups may be the most suitable for use as the peptide linker motif.

Based on this background, we have investigated a method to effectively introduce carboxy groups onto a Ti surface by modification of the Ti surface chemistry through different degrees of Au sputtering. The effect of Au sputtering on the binding of ω-mercapto-1-alkanoic acid type linker molecules was evaluated using a combination of X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). The null hypothesis was that the introduction of carboxy groups onto the Ti substrate would not be enhanced by Au modification of the Ti surface.

MATERIALS AND METHODS

Specimen preparation
Second grade pure titanium plate (TP340; 1 mm thick,
Tokyo Titanium, Saitama, Japan) was cut into 10×10 mm² pieces (Ti plates), and sand-blasted with Al₂O₃ (70 μm average particle diameter) for 5 s at 0.5 MPa to simulate the surface-abrasion of an implant post so as to enhance the biological affinity. The surface roughness value (Rₐ) of the sand-blasted Ti plates was 0.74±0.03 μm, which was nearly twice as large as the Rₐ before the sandblasting. The plates were then sonicated in acetone, 30% nitric acid, and distilled water in this order for 10 min each. After drying, the Ti plates were Au sputtered for 5, 10, 20, 50, 100 and 200 s at 10 mA under 10 Pa Ar gas using an ion coater (E-1030, Hitachi, Tokyo, Japan). A Ti plate that was not Au sputtered was used as a reference. The Ti plates were then immersed in a 2 mM solution of 12-mercaptododecanoic acid (HS-C₁₁-COOH; Sigma-Aldrich, St. Louis, USA) in ethanol for 2 h. After rinsing the treated surface sequentially with ethanol and distilled water (1.5 mL, three times for each by a pipette), the specimens were dried in a vacuum desiccator.

X-ray photoelectron spectroscopy (XPS)

Elemental analysis of the Ti specimen surface was conducted before and after HS-C₁₁-COOH treatment using XPS (AXIS-HSi, Kratos, Manchester, UK). The XPS measurement conditions were as follows: vacuum of 5.3×10⁻⁷ Pa, acceleration voltage of 15 kV, emission current of 10 mA, monochromatic Al Kα radiation, hybrid mode with 300×700 μm² analysis area. Pass energies of 160 and 40 eV were used for the wide and narrow scan modes, respectively. The binding energy scale was calibrated according to the C 1s peak (284.8 eV). The Ti substrate and sputtered Au layer were assessed according to the Ti 2p and Au 4f peaks, respectively, and the bound HS-C₁₁-COOH according to the S 2p, C 1s, and O 1s peaks.

Fourier transform infrared spectroscopy (FTIR)

The binding of HS-C₁₁-COOH onto the Au-sputtered Ti specimen surface was examined using FTIR spectroscopy (Spectrum One, Perkin-Elmer Japan, Yokohama, Japan) with the diffuse reflection method and 16 accumulations. The IR absorption bands of carboxy (C=O stretching around 1,760 cm⁻¹) and methylene (C-H stretching around 2,900 cm⁻¹, bending around 1,400–1,200 cm⁻¹) groups were monitored.

RESULTS

Relative Au content on the Ti plate

Five elements (Ti, Au, S, C, O) were assumed to be the main contributors to the XPS spectrum, and the relative atomic contents (at%) of each were estimated using the band intensity of each element. Note that the contribution from contaminants to the C content was subtracted to calculate the relative content of each element.

Figures 1a and b show XPS spectra for Au 4f and Ti 2p, respectively, on Ti plates that were Au sputtered for 5–200 s. Longer sputtering times led to stronger Au intensity and weaker Ti intensity; the Ti peak disappeared after 100 s sputtering. Figure 2 shows the relative content (at%) of Au and Ti as a function of the Au sputtering time. The purpose of this study is to control the binding rate of the linker by modification of the Ti surface through Au sputtering. Therefore, we considered the change in the relative area occupied by Ti and Au during Au sputtering. The Au coverage is defined by equation (1) on the assumption of a Ti-Au binary system:

\[
\text{Au coverage (%)} = \frac{\text{Au at%}}{(\text{Au at%} + \text{Ti at%})} \times 100 \quad (1)
\]

The apparent Au coverage on the Ti plate was estimated as a function of the sputtering time and the dependence of the Au coverage on the sputtering time is shown in Fig. 3. The coverage increased over time to 26% (5 s), 93% (50 s) and 98% (100 s).

XPS and FTIR analyses of the Au-sputtered Ti plates to which HS-C₁₁-COOH was applied

Figure 4 shows XPS spectra (S 2p and C 1s peaks) for
Au-sputtered (100 s) Ti plates before and after immersion in the HS-C$_{11}$-COOH solution. The S 2p band was observed only after immersion and consisted of two peaks at 162.0 and 163.2 eV (Fig. 4a). The C 1s peak at 284.8 eV was present before immersion and was tentatively assigned to a C-C or C-H structure due to trace amounts of contaminants (Fig. 4b). After immersion, the C 1s peak intensity doubled, and another peak appeared at 289.5 eV, which was assigned to the -COO$^-$ group.

Figure 5 shows XPS spectra for the O 1s band observed on Au-sputtered (5, 20, and 100 s) Ti plates before and after immersion in the HS-C$_{11}$-COOH solution. Prior to immersion, two peaks were observed for the 5 s Au-sputtered Ti plates (Fig. 5a), where the Au coverage was low (Fig. 2). The peak at 530.0 eV was assigned to O$_2^-$ from titanium oxide and that at 532 eV to OH$^-$ on the oxide surface. For the Ti plates that were Au sputtered for 20 s, the intensity of the O 1s peaks decreased, and that for the O$_2^-$ peak was greater. The peak intensities decreased further and the O$_2^-$ peak disappeared after a longer Au sputtering time (100 s).

Similar features were observed after the Au-sputtered Ti was treated with HS-C$_{11}$-COOH, in that the O$_2^-$ peak was significantly decreased and the OH$^-$ peak became more prominent (Fig. 5b).

The dependence of the relative contents of Au, Ti, S, C and O on the Au coverage is shown in Fig. 6. While the relative Au content on the Ti plates increased with Au coverage (Fig. 6a, open circles), it became lower after immersion in the HS-C$_{11}$-COOH solution (Fig. 6a, filled circles). The relative Ti content decreased with the Au coverage (Fig. 6b, open circles), although it decreased slightly further after immersion in the HS-C$_{11}$-COOH solution (Fig. 6b, filled circles). The relative S content after immersion increased with Au coverage (Fig. 6c, filled circles). The relative C content increased up to 76–93% Au coverage and then decreased (Fig. 6d). This feature was common for the specimens before and after immersion. The Au coverage dependence of the relative O content (Fig. 6e) was almost the same as that for Ti; the relative O content decreased with Au coverage and was further decreased after immersion.
Figure 5 shows the FTIR spectrum of a 100 s Au-sputtered Ti plate after immersion in HS-C_{11}-COOH. The band at 1,619 cm$^{-1}$ was assigned to the C=O stretching motion in the carboxy group and bands at 1,400 and 1,248 cm$^{-1}$ were assigned to the bending motion of the methylene groups, each in the bound HS-C_{11}-COOH molecule.

**DISCUSSION**

Methods for the biofunctionalization of the Ti surface and the current experimental perspective

Biofunctionalization of metallic material surfaces typically involves the introduction of polymeric components. One example is silanization$^{1}$, where a NiTi plate was immersed in aqueous γ-aminopropyltriethoxysilane, polymerized at 100°C and coupled with glutaraldehyde to fix the human plasma fibronectin. Another example is plasma thermal spraying$^{10}$, in which a Ti plate was plasma sprayed by the glow discharge in allylamine gas, followed by consecutive immersion in glutaraldehyde and type I collagen solutions. An example of the electrodeposition method involved the immersion of a Ti plate in a saline solution of polyethylene glycol (PEG) with an NH$_2$ group at its end to electrodeposit PEG$^{11}$.

While we chose the sputtering method onto flat substrate surface aiming to control the degree of Au...
coverage simply by the sputtering time, electrolytic plating or sputtering with tilt and/or rotary sample holder may be better choices for complicated surface geometry like dental implant fixtures. Recently, “polygonal barrel-sputtering” method has been developed to effectively form a uniform film, where specimens are sputtered in a rotating polygonal barrel. The advantage of the method we adopted is that a wide choice of alkanethiols with various terminal functional groups is available, by which the surface may be optimized for binding to target substances. Moreover, the S-Au bond energy, which correlates to the stability of the bond formed between the substrate and the linker, is as high as 44 kcal/mol (184 kJ/mol) (quasicovalent bond), which is comparable to the covalent C-C bond energy of 83 kcal/mol (347 kJ/mol). With an aim to fix certain proteins on Ti implants via peptide bonding, 12-mercaptopodocanoic acid (HS-C\textsubscript{11}-COOH) was selected as a promising alkanethiol-type linking agent. To determine the effect of Au sputtering on attachment of the alkanethiol, the alkanethiol concentration and the substrate immersion time were fixed at 2 mM and 2 h, respectively, and the sputtering time was varied.

The phenomena that occurs during treatment of the Ti substrate is discussed in the following sections based on the relative atomic content (at%) on the Ti substrate surface and the chemical state determined by XPS and FTIR analyses.

Effect of surface roughness of the specimen on the analysis
In this study, sand-blasted Ti plates were used as substrates. The surface roughness of the specimen might influence the results of XPS analysis. In XPS measurement, the intensity of the photoelectron from an ideally flat surface depends on an angle between the normal line to the sample and the detector direction. On a rough surface, however, the detected intensity may become weakened because the direction of photoelectron emission is not uniform due to the rough surface. Insulating materials (non-conductive materials) may also cause heterogeneous charging. However, assuming that the surface roughness of each Ti plate used was identical, it might be possible to compare the relative intensity. The degree of alkanethiol adsorption might be affected by the surface roughness. But we thought it did not become an artifact in the current diffuse reflection IR analysis because the analytic samples were collected from the surface as powders by scratch pins. So, it was assumed that the IR analysis did not depend on the surface roughness.

Au coverage on the Ti surface
The relative Au coverage was ca. 25% after 5 s sputtering, which then increased to ca. 50% after 10 s, over 90% at 50 s, and exceeded 98% at 100 s (Fig. 3). However, it should be noted that besides the uncovered Ti, the Ti beneath the formed Au layer may also be detected to a finite depth (a few nanometers) due to the limitations inherent to the instrument. This would lead to a lower calculated Au coverage using Eq. (1), and the effect would be more serious for shorter sputtering times since the sputtered Au layer would be thinner. Thus, the relative Au content would be higher than that observed for a shorter sputtering time. The linear relation between the Ti and Au content (data not shown) indicates that the Ti surface became covered with Au during the sputtering process.

Quality of the deposited Au layer
We used a handy “coater” for the Au sputtering onto Ti plates. In this case, the quality of the deposited Au layer might be inferior to those formed under more strict condition (higher vacuum). Actually, there appeared a C band in the XPS measurement even for the Ti plate without the HS-C\textsubscript{11}-COOH treatment. It was possible that some organic contaminant remained in the low vacuum environment with our system.

Furthermore, the chemical species type of the Ti substrate surface must influence the interaction between the substrate and Au sputtered on it. Figure 8 (constructed from Figs. 6b and 6e) shows a relation between the relative contents of O and Ti. The linear relation ($R^2=0.9816$) suggests that Ti existed as some stoichiometric oxide species rather than a pure metallic form. The coater used in this study might have provided insufficient vacuum for keeping the Ti surface from oxidation. It was reported that the surface oxide layer hindered the intimate contact of different metals\textsuperscript{15}. Thus, we supposed that the attachment of the sputtered Au was weaker on the oxide Ti than expected on the pure Ti surface.

Nevertheless, we believe that the Au sputtering in this study was still effective, at least partly, to enhance the attachment of the alkanethiol (HS-C\textsubscript{11}-COOH), from the analogy to the priming in the use of resin cements. That is, while the adhesive monomers in the primer only weakly bind to the adherend surface through hydrogen bond or van der Waals force, they are essential in that they enhance the surface affinity to the bonding
monomers. As for the binding strength itself, it should be made clear and improved in future.

**Binding of HS-C\textsubscript{11}-COOH**

After immersion in the HS-C\textsubscript{11}-COOH solution, the characteristic S, C and O elements on each Ti specimen were assessed. Among these elements, S is unique and only expected to originate from the alkanethiol (HS-C\textsubscript{11}-COOH). To enhance the features of both the gold coverage on the Ti plate and the alkanethiol treatment, a new plot was constructed from the data in Figs. 3 and 6, in which the differential S content on the substrate before and after immersion is plotted as a function of the gold coverage (Fig. 9). The attached S content increased with the degree of gold coverage. A linear regression of this plot gave a relatively high value of $R^2$ (0.9632), which indicates that the attachment of the sulfide-type linking agent to the Ti surface was linearly enhanced by Au modification of the Ti surface. In Fig. 4a, two S 2p bands were found, of which the band located at 162.0 eV was assigned to a bound thiol (Au-S)\textsuperscript{16-19}. The higher energy band at 163.2 eV corresponds to that for unbound thiol\textsuperscript{19}. However, the intensity was half that of the lower energy band, which corresponded to the photoionization cross section ratio (2:1) of S 2p\textsubscript{3/2} and S2p\textsubscript{1/2} doublet peaks for 2p. This indicates that most of the S detected is from the bound thiol.

The carbon peak (284.8 eV) due to contaminant hydrocarbons (C-C, C-H) was detected in the C 1s spectrum (Fig. 4b). After immersion, two bands were observed; a higher energy band at 289.0 eV assigned to the carboxy group and a lower energy band (284.8 eV) assigned to C-C and C-H (methylene group) in the HS-C\textsubscript{11}-COOH molecule (Fig. 4b). In addition, the peak intensity of the latter (hydrocarbons) was twice as high as that observed for the specimen before immersion. These results indicate that the linking agent is bound to the Au-sputtered surface.

However, it is difficult to determine any precise information from the relative O content data for the bound alkanethiol, partly because the contribution from titania was far more dominant than the small amount of carboxy oxygen in the bound HS-C\textsubscript{11}-COOH. As the Au sputtering time was increased, the relative Ti and O contents decreased concomitantly (Fig. 6). Thus, the major oxygen source is attributed to the titania present on the Ti plate surface. However, the O 1s spectra (Fig. 5) revealed two bands before immersion, which would be attributed to oxygen in titania (530.0 eV) and OH\textsuperscript{−} in the surface layer of the oxide (532.0 eV). The intensity of these peaks was larger for shorter sputtering times. After immersion, while the intensity of the titania oxygen peak weakened, the OH\textsuperscript{−} peak intensity remained unchanged or even increased for a Au sputtering time of 100 s. This indicates that the intensity of the sublayer oxide peak decreased as the Ti substrate was covered by the HS-C\textsubscript{11}-COOH adlayer, accompanied by an increase in the OH\textsuperscript{−} peak intensity; therefore, the OH\textsuperscript{−} is related to the carboxy group in the HS-C\textsubscript{11}-COOH molecule.

The IR band assignments (CH\textsubscript{2} and COOH groups) suggested the binding of some aliphatic carboxylic acid, which is consistent with the chemical structure of HS-C\textsubscript{11}-COOH. Therefore, the IR data also supports the attachment of the alkanethiol to the Au-modified Ti surface.

**Controlled Ti surface functionalization by Au sputtering**

The binding of HS-C\textsubscript{11}-COOH on the Au-modified Ti substrate was controlled by the Au coverage. Considering that the Ti surface was gradually covered by Au over the sputtering time and was mostly covered by Au after 100 s (Fig. 3), the degree of HS-C\textsubscript{11}-COOH binding may be adjustable up to 100 s sputtering under the current sputtering conditions employed. Thus, Au sputtering onto the Ti surface would be suitable for
alkanethiol treatment, and this could be a candidate method for the effective modification of a Ti surface to improve biocompatibility.

Alkanethiol type 12-mercaptododecanoic acid (HS-C$_{11}$-COOH) was selected as the protein-linking agent in this study. However, the results may differ for alkanethiols with different alkyl chain lengths or different terminal functional groups (e.g., amino groups). Therefore, other alkanethiols should also be examined to determine appropriate alkanethiol linking agents that are suitable to fix proteins that will accumulate the target cells.

CONCLUSIONS

Titanium plates were Au sputtered for various periods, immersed in a solution of alkanethiol with a carboxy group end (HS-C$_{11}$-COOH), and analyzed using XPS and FTIR techniques to determine if Au sputtering could enhance the alkanethiol treatment of a Ti surface. The following conclusions were obtained.

1. The gold coverage increased with the sputtering time: 90% after 50 s and >98% after 100 s.
2. The difference in the S, C, and O contents before and after immersion in the alkanethiol solution increase with the Au sputtering time, which indicated successful attachment of the alkanethiol molecules.
3. XPS spectral analysis for S 2p, C 1s, and O 1s after immersion in the alkanethiol solution indicated Au-S, COO$^-$, and OH$^-$ species, which implies the attachment of alkanethiol molecules on the Au-sputtered Ti surface.
4. FTIR spectra revealed peaks assignable to an aliphatic carboxylic acid after immersion, which indicated the binding of alkanethiol molecules onto the modified Ti surface.
5. A strong positive correlation was observed between the relative S content and the Au coverage, which indicated that Au sputtering is effective for modification of a Ti substrate with alkanethiol type molecules.

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