Formation and Stability of Self-Assembled Monolayers on Cobalt-Chromium alloy

Gopinath Mani, Marc D. Feldman, Sunho Oh, C. Mauli Agrawal.

Department of Biomedical Engineering, The University of Texas at San Antonio

Introduction: Surface modification of metals using self-assembled monolayers has several potential biomedical applications. However, most studies have been carried out on model substrates such as gold or silicon.[1] Both gold and silicon are rarely used as biomaterials because of their insufficient mechanical properties and poor biocompatibility. Titanium, stainless steel, and cobalt-chromium alloys are the metals that are commonly used for medical implants. SAM coatings have been previously reported on these engineering biomaterials[2] except on cobalt-chromium (Co-Cr) alloys. In this study, for the first time, SAMs were coated on a Co-Cr-W-Ni alloy using octadecyltrichlorosilanes (OTS) and their stability was investigated under physiological conditions for up to seven days.

Methods: The Co-Cr-W-Ni alloy (Haynes 25) substrate (L605 grade) was purchased from High Tech Metals, Inc (Sylmar, CA). A thin Co-Cr-W-Ni alloy film was also prepared by sputter coating the glass slides with 50 nm thick layer of alloy. Both sputtered thin alloy films (*sp*-Co-Cr) and bulk metal (*bulk*-Co-Cr) specimens were used for all the experiments. The *sp*-Co-Cr and *bulk*-Co-Cr specimens were immersed in 3 mL of 1 mM OTS in anhydrous toluene for 3 hours. The specimens coated with OTS SAM were briefly rinsed in anhydrous toluene followed by sonication in the same solvent for 10 minutes. The specimens were then rinsed in copious amount of running dd-H_2O and dried using N_2 gas. OTS SAM coated *sp*-Co-Cr and *bulk*-Co-Cr specimens are referred to here as SAM/sp-Co-Cr and SAM/bulk-Co-Cr, respectively. SAM/*sp*-Co-Cr and SAM/*bulk*-Co-Cr specimens were immersed in 3 mL of 20 mM tris-buffered saline (TBS) (pH = 7.4) and incubated at 37 °C for up to 7 days. The specimens were then taken out and rinsed in dd-H_2O followed by N_2 gas drying. The specimens were characterized using contact angle goniometry, fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS).

Results/Discussion: The static contact angles measured for *sp*-Co-Cr, SAM/*sp*-Co-Cr, *bulk*-Co-Cr and SAM/*bulk*-Co-Cr were 32.8 ± 3.3°, 73.3 ± 7.7°, 112.4 ± 0.9°, and 111.5 ± 2.9°, respectively. This significant increase in the contact angle value after OTS treatment suggests the formation of ordered monolayers terminated with $–CH_3$ groups on Co-Cr alloy. The FTIR peaks for the symmetric and asymmetric stretching vibrational modes of methylene groups were observed at 2849 cm^{-1} and 2916 cm^{-1}, respectively (Figure 1). This strongly suggests the formation of well-ordered monolayers on Co-Cr alloy. Figure 2 shows the AFM tapping mode height images of sputtered and bulk Co-Cr before and after SAM deposition. The typical height and diameter of the OTS islands on *sp*-Co-Cr were ~2.6 nm and ~60 nm, respectively. The bulk metal was covered with islands of larger sizes (~150 nm) with a typical height of ~2.4 nm. The theoretical length of fully extended OTS molecules in the all-trans conformation is 2.62 nm. This indicates that the hydrocarbon chains of OTS molecules are oriented perpendicular to the surface. The XPS O 1s peaks at 531.0 eV and 532.6 eV after SAM deposition suggest the formation of Si-O-Metal and Si-O-Si bonds, respectively (Figure 3). No significant differences in the contact angle, FTIR, and XPS data were observed for both *sp*-Co-Cr and *bulk*-Co-Cr after immersion in TBS at 37 °C for 7 days.

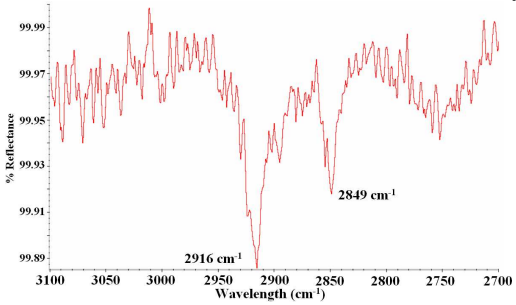

Figure 1. FTIR spectrum of OTS SAM coated Co-Cr.

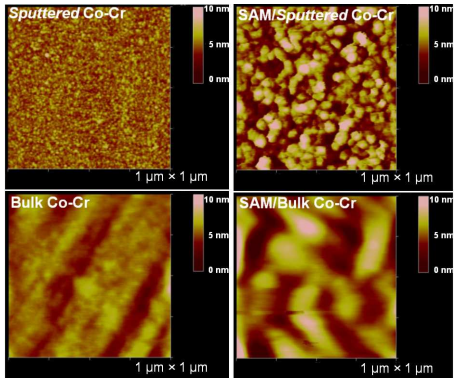

Figure 2. AFM height images of sputtered and bulk Co-Cr before and after SAM deposition.

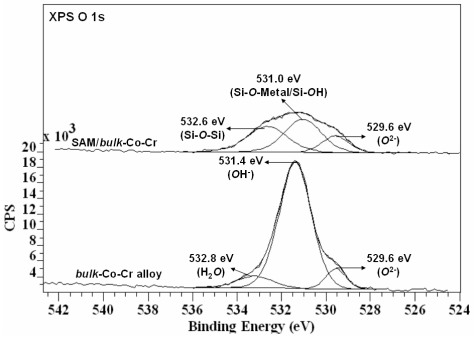

Figure 3. XPS O 1s spectra of Co-Cr before and after SAM deposition.

Conclusions: SAMs of OTS were successfully coated on both sputtered and bulk Co-Cr alloy. These monolayers remained ordered and bound to the alloy surface under physiological conditions for 7 days. Thus, this study demonstrated a stable SAM system on Co-Cr alloy for potential biomedical applications such as drug delivery.[3]

References: (1) Ulman A, Chem. Rev 1996, 96, 1533-1554. (2) Gawalt ES, Langmuir 2001, 17, 5736-5738. (3) Mani G, Biomaterials 2008, 29, 4561-4573.