

Oxidative and In-Vitro Stability of Alkanethiol Self Assembled Monolayers (SAMs) on 316L Stainless Steel

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Introduction: Bare metal coronary stents have reduced angiographic restenosis by providing scaffolding that diminishes vessel recoil and negative remodeling. However, neo-intima formation leads to in-stent restenosis which limits the long term benefit of coronary stents.¹ Attachment of therapeutic drugs to SAMs after their assembly on 316L stainless steel (SS) (currently used for stents) could possibly serve as a localized drug delivery system, which, if used in coronary stents, could reduce arterial restenosis. It could also minimize or eliminate some of the problems with current technologies such as allergic reactions to the polymers used on stents for drug delivery. SAMs formed on SS are not as well studied as gold. Few studies have thoroughly investigated the oxidative and *in vitro* stability of SAMs. No literature reporting the *in vitro* stability of SAMs on 316L SS was found. To fully exploit the biomedical applications of SAMs on 316L SS, the stability of these SAMs needs to be evaluated.

Materials and Methods: 316L SS sample plates (20mm x 20mm x 2mm, ESPI Corp. Inc.) were polished (final roughness $0.2 \pm 0.1 \mu\text{m}$), cleaned chemically (ultrasonicated for 10 min each in 70 % ethanol, acetone and 40 % nitric acid) and subjected to glow discharge gas plasma (GDGP) treatment (Harrick Scientific, NJ) for 3 min (O_2 environment, 15 psi). The plates were immediately dipped in amphiphile solutions (10 mM ethanolic solution) of 1-dodecanethiol ($-\text{CH}_3$ SAM) for 48hr to form methyl terminated SAMs, used as a model alkanethiol SAM for stability studies. These SAMs were then exposed to room temperature (oxidative) and phosphate buffered saline (PBS) (*in vitro*) to evaluate their stability at 1, 3, 7, 14, 21, 28 days. The samples were characterized using X-ray photoelectron spectroscopy (XPS), fourier transform infrared spectroscopy (FTIR) and contact angle measurements

Results and Discussion: Detailed characterization of formation of $-\text{CH}_3$ SAM on 316L SS has been described elsewhere². FTIR spectra of $-\text{CH}_3$ SAM on 316L SS showed the CH_2 vibrations of the alkyl chains of the SAMs at 2917 and 2846 cm^{-1} respectively. The XPS spectra [C (1s) region] of the $-\text{CH}_3$ SAM showed a photoelectron peak centered at 284.7 eV, which is characteristic of the carbon 'C' of the methylene chain ($\text{CH}_2\text{CH}_2\text{CH}_2$). Thus FTIR and XPS spectra validated the formation of SAMs on 316L SS.

Figure 1 shows the oxidative (Figure 1a) and PBS (Figure 1b) stability over time. Figure 1 shows the S (2p) region of $-\text{CH}_3$ SAM on 316L SS. The peak at 163 eV represents the S ($2p_{3/2}$) metal thiolate peak, which falls within the range (160-165 eV) for thiol SAMs and is consistent for thiol SAMs adsorbed on copper, silver, gold

and iron.³ The peak at 168.5 eV represents the S (2p) peak for oxidized sulphur (sulphonates).⁴ The spectra represent relative values and have been offset for clarity. Over time (oxidative and PBS exposure) we see the strength of the sulphonate peak (168.5 eV) increasing while the strength of the metal thiolate peak (163 eV) decreasing. After 14 day we see the complete absence of the metal thiolate peak. During oxidative exposure the SAMs remain on the metal as oxidized species in the form of sulphonates. However, the long term immersion of SAM in PBS causes the SAM not only to get oxidized but they also get completely desorbed (absence of sulphonate peaks) and possibly washed in the solution hence after 21 days immersion we see no sulphur peaks whatsoever.

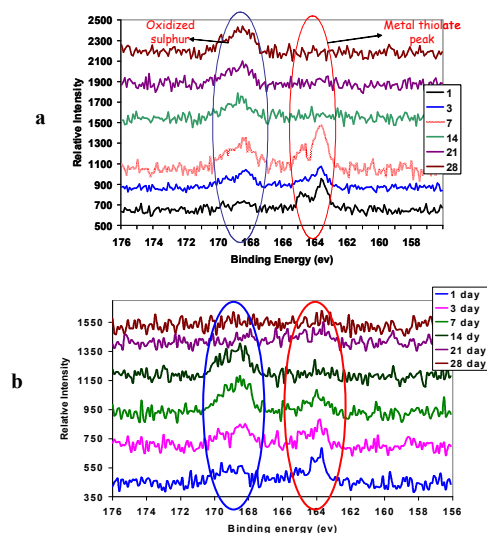


Figure 1: Sulphur 2p XPS spectra; Stability with time of $-\text{CH}_3$ terminated $[\text{CH}_3(\text{CH}_2)_{11}\text{SH}]$ alkanethiol SAMs. (a) oxidative stability and (b) PBS stability. The spectra represent relative values and have been offset for clarity.

Conclusions: Alkane thiol SAMs oxidize completely within 14 days. The SAMs tend to desorb and leave the metal surface after longer time periods (21 days) in PBS immersion, while for oxidative exposure the SAMs continue to be attached on the metal surface in the form of sulphonates. Engineering for improved stability of alkane thiol SAMs is currently underway to ensure their viability for the chosen biomedical applications.

References:

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