Stability of Self-Assembled Monolayers on Titanium for Biomedical Applications

Gopinath Mani[1,2], David M. Johnson[1], Denes Marton[2], Victoria Dougherty[1],
Marc Feldman[2], Devang Patel[2], Arturo Ayon[1], and C.Mauli Agrawal[1,2].
[1]The University of Texas at San Antonio, [2]The University of Texas Health Science Center at San Antonio.

Introduction: The use of Self-Assembled Monolayers (SAMs) to modify the surface chemistry of engineering biomaterials is increasing rapidly [1]. A variety of biomolecules have been immobilized on metals using SAMs [1,2,3]. However, the studies on the stability of SAMs under physiological conditions are limited especially for a commonly used biomaterial like titanium (Ti). Here, we have investigated the stability of phosphonic acid SAMs on titanium under *in-vitro*, shelf storage, and sterilization conditions.

Methods: Hydroxyl-terminated SAMs were formed by immersing sputter coated Ti substrates in 2mM solutions of (11-hydroxylundecyl) phosphonic acid in double-distilled water (dd-H_2O) for 60 hours. The stability of these SAMs was investigated under the following conditions at 1, 7, 14, 21, and 30 days: (a) immersion in tris-buffered saline (TBS) solution at 37°C (b) immersion in dd-H_2O at room temperature (c) exposure to ambient laboratory conditions (ALC) (d) exposure to UV light for 1 and 12 hours. The samples were characterized using X-ray photoelectron spectroscopy (XPS) and contact angle measurements (CAM) at all time points.

Results / Discussion: In Fig. 1, the XPS O 1s peak at 530.2 eV belongs to TiO_2. The peaks at 531.4 eV and 533 eV are assigned to P-O-Ti/P=O and P-O-H/C-O-H, respectively. The ratio between the peaks at 531.4 eV and 533 eV is 2, which suggests the conversion of P-O-H bonds to P-O-Ti bonds. This indicates the covalent attachment of SAMs on Ti. The CAM of these SAMs were 54.6° ± 2°.

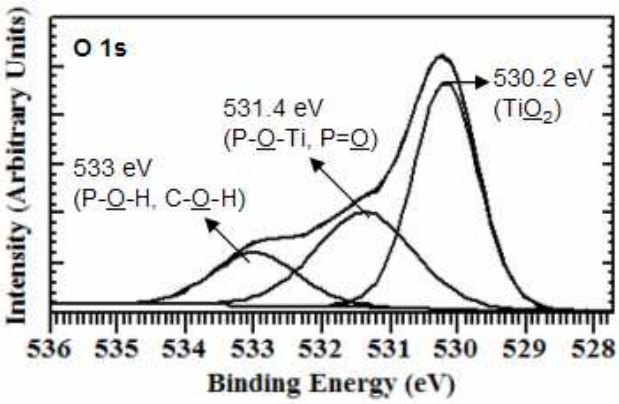

Figure 1. High resolution XPS O 1s spectrum for phosphonic acid SAMs on Ti

Fig. 2 shows the change in the elemental concentrations of SAMs formed on Ti in TBS at different time points. The decrease of the carbon and phosphorous concentrations and the increase of the Ti concentration suggest desorption of SAMs in *in-vitro* conditions. The P 2p/Ti 2p and C 1s/Ti 2p ratios suggest the desorption of SAMs occurs during the first 14 days but not during the remaining period (till 30 days). Similar behavior was observed during the immersion in dd-H_2O.

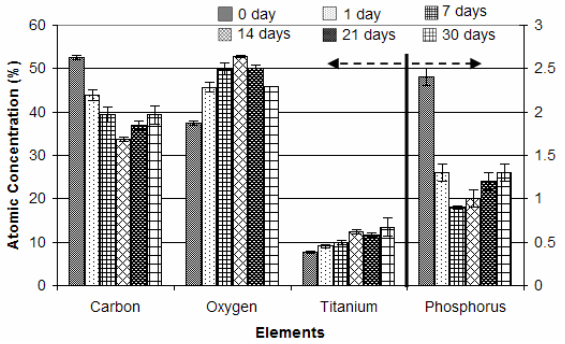

Figure 2. XPS-determined atomic conc. of the SAMs formed Ti after its incubation in TBS at 37 °C

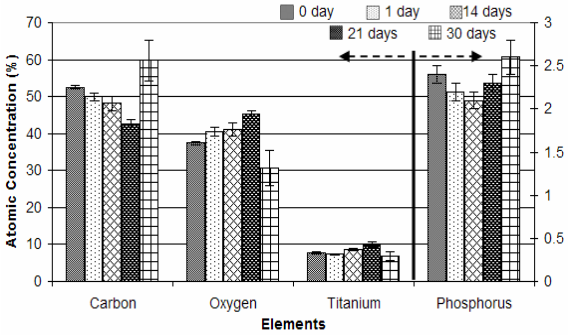

Figure 3. XPS-determined atomic conc. of the SAMs formed Ti after its exposure to ALC

In Fig. 3, the P 2p/Ti 2p and C 1s/Ti 2p ratios suggest minimal desorption of SAMs up to 21 days under ALC. Exposure to UV light oxidizes the hydrocarbon chain in the SAMs leaving phosphonate groups on Ti at 12 hours (Fig. 4).

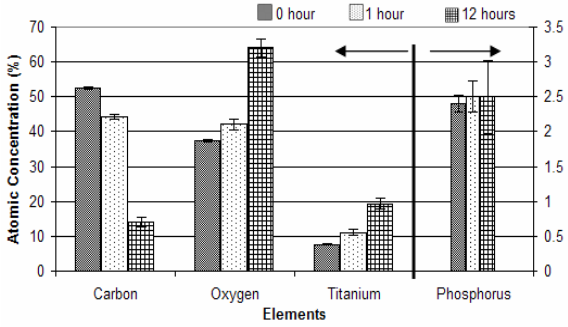

Figure 4. XPS-determined atomic conc. of the SAMs formed Ti after its exposure to UV light

Conclusions: Phosphonic acid SAMs on Ti are more stable in ALC than in TBS at 37°C and in dd-H_2O. Desorption of SAMs was observed for first 14 days in TBS and dd-H_2O. However, after this initial desorption period, not much of the SAMs were desorbed up to a month. This behavior is more pronounced in TBS than in dd-H_2O. Sterilization using UV light may be a challenge for SAMs coated Ti.

References: (1) Annu. Rev. Biophys. Biomol. Struct. 1996; 25:55-78 (2) Langmuir 2003; 19:200-204 (3) Langmuir 2006; 22:8197-8204