

REDUCTIVE DESORPTION OF SELF-ASSEMBLED MONOLAYERS OF OCTADECYL PHOSPHATE (ODP) FROM TI/TiO₂ SURFACES

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INTRODUCTION: Self-assembly of alkylphosphate is a powerful approach to modify various surface properties of titanium (Ti) and titanium oxide (TiO_x), which enables extended applications of Ti-based materials in biosensors and corrosion-resistant systems etc.^{1,2} Electrochemical reductive desorption has been established as a useful way to examine the electrochemical properties as well as surface coverage of self-assembled monolayers (SAM), mostly thiol-based SAM on gold.^{3,4} By applying this methodology to *n*-octadecylphosphoric acid (ODP) SAM formed on Ti(metal) surface, we attempt to broaden our understanding of the surface coverage and bind characteristics of ODP films on Ti surfaces.

METHODS: (1) *Sample preparation:* Ti (metal) substrates were prepared by physical vapor deposition (PVD) onto silicon wafers as previously reported.² The self-assembled monolayer of *n*-octadecyl phosphoric acid (ODP) was generated by immersing a Ti(metal) substrate in a organic solvent (mixture of *n*-heptane and propan-2-ol, 100:4 v/v ratio) containing ODP with a concentration of 500 μM. (2) *Monolayer characterization:* Formation of ODP self-assembled monolayer was confirmed by water contact angle measurement (~105° static contact angles), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). (3) *Cyclic voltammetry:* Cyclic voltammetry was performed in a three electrode cell (working electrode: ODP SAM-coated Ti metal, reference electrode: Ag/AgCl(sat'd), and counter electrode: Pt) using a potentiostat (AMEL Instruments, Model 2053). The scan rate was 20 mV/sec and all the measurements were performed under pH 12 condition (adjusted by NaOH).

RESULTS: A representative cyclic voltammogram of reductive desorption ODP SAM from Ti(metal) surface is presented in Figure 1. In this figure, the first and the second forward potential scans (zero to negative potential) of ODP SAM, together with that of a bare Ti substrate are presented. The cathodic currents starting from ~0.5V at bare Ti substrate, which is attributed to H₂ evolution, is considerably reduced by ODP SAM and the commencement of the H₂ evolution is delayed to ~1.0V. The broad shoulder peak at ~ 1.5V is attributed to the desorption of ODP films from Ti (metal) surface.

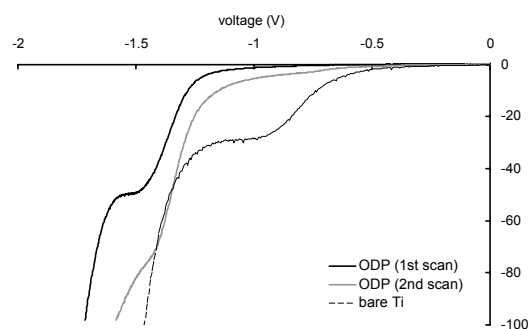


Fig. 1: A representative cyclic voltammogram of reductive desorption of ODP SAM from Ti(metal) surface.

DISCUSSION & CONCLUSIONS: The total (or observed) currents during potential scan are composed of (a) double layer charging (b) H₂ evolution (c) desorption of ODP

$$Q_{\text{tot}} = Q_{\text{dl}} + Q_{\text{H}_2} + Q_{\text{des}}$$

Through a quantitative analysis method suggested by T. Kawaguchi et al,⁴ we extracted the currents due to desorption process of ODP film, Q_{des} , and they were further used to estimate the ODP film coverage on Ti (metal) surface. In contrast to alkanethiols, which bind exclusively as monodentate on gold surface, a mixture of monodentate and bidentate (or even tridentate) coordination of alkylphosphate on Ti (metal) surface leads to a complicated interpretation of surface coverage based upon this method. The surface coverage of ODP on Ti (metal) surface will be discussed in comparison with *n*-alkanethiols on gold surfaces.

REFERENCES: ¹M. Textor, et al (2000) *Langmuir* **16**:3257-71. (2000) ²S. Tosatti, et al (2002) *Langmuir* **18**:3537-48. ³C.A. Widrig, et al (1991) *J. Electroanal. Chem.* **310**:335-59. ⁴T. Kawaguchi, et al (2000) *Langmuir* **16**:9830-40.