

Fabrication of Highly Stable Low-Density Self-Assembled Monolayers by Thiolyne Click Reaction

Authors : Leila Safazadeh, Brad Berron

Abstract : Self-assembled monolayers have tremendous impact in interfacial science, due to the unique opportunity they offer to tailor surface properties. Low-density self-assembled monolayers are an emerging class of monolayers where the environment-interfacing portion of the adsorbate has a greater level of conformational freedom when compared to traditional monolayer chemistries. This greater range of motion and increased spacing between surface-bound molecules offers new opportunities in tailoring adsorption phenomena in sensing systems. In particular, we expect low-density surfaces to offer a unique opportunity to intercalate surface bound ligands into the secondary structure of proteins and other macromolecules. Additionally, as many conventional sensing surfaces are built upon gold surfaces (SPR or QCM), these surfaces must be compatible with gold substrates. Here, we present the first stable method of generating low-density self assembled monolayer surfaces on gold for the analysis of their interactions with protein targets. Our approach is based on the 2:1 addition of thiol-yne chemistry to develop new classes of γ -shaped adsorbates on gold, where the environment-interfacing group is spaced laterally from neighboring chemical groups. This technique involves an initial deposition of a crystalline monolayer of 1,10 decanedithiol on the gold substrate, followed by grafting of a low-packed monolayer on through a photoinitiated thiol-yne reaction in presence of light. Orthogonality of the thiol-yne chemistry (commonly referred to as a click chemistry) allows for preparation of low-density monolayers with variety of functional groups. To date, carboxyl, amine, alcohol, and alkyl terminated monolayers have been prepared using this core technology. Results from surface characterization techniques such as FTIR, contact angle goniometry and electrochemical impedance spectroscopy confirm the proposed low chain-chain interactions of the environment interfacing groups. Reductive desorption measurements suggest a higher stability for the click-LDMs compared to traditional SAMs, along with the equivalent packing density at the substrate interface, which confirms the proposed stability of the monolayer-gold interface. In addition, contact angle measurements change in the presence of an applied potential, supporting our description of a surface structure which allows the alkyl chains to freely orient themselves in response to different environments. We are studying the differences in protein adsorption phenomena between well packed and our loosely packed surfaces, and we expect this data will be ready to present at the GRC meeting. This work aims to contribute biotechnology science in the following manner: Molecularly imprinted polymers are a promising recognition mode with several advantages over natural antibodies in the recognition of small molecules. However, because of their bulk polymer structure, they are poorly suited for the rapid diffusion desired for recognition of proteins and other macromolecules. Molecularly imprinted monolayers are an emerging class of materials where the surface is imprinted, and there is not a bulk material to impede mass transfer. Further, the short distance between the binding site and the signal transduction material improves many modes of detection. My dissertation project is to develop a new chemistry for protein-imprinted self-assembled monolayers on gold, for incorporation into SPR sensors. Our unique contribution is the spatial imprinting of not only physical cues (seen in current imprinted monolayer techniques), but to also incorporate complementary chemical cues. This is accomplished through a photo-click grafting of preassembled ligands around a protein template. This conference is important for my development as a graduate student to broaden my appreciation of the sensor development beyond surface chemistry.

Keywords : low-density self-assembled monolayers, thiol-yne click reaction, molecular imprinting

Conference Title : ICCPE 2015 : International Conference on Chemical and Process Engineering

Conference Location : London, United Kingdom

Conference Dates : January 19-20, 2015