Characterization of SAM Adsorption on Surfaces Made of Arrays of Skyscraper Nanopillars

Venkataramani Anandan, Rajan Gangadharan and Guigen Zhang
Department of Bioengineering, Clemson University, Clemson, SC 29634, USA

Statement of Purpose: Self assembled monolayers (SAMs) of molecules are commonly used for surface modification of many biomaterials. One such example is use SAM alkanethiols to facilitate the functionalization of nanostructure modified electrodes made of inorganic conducting materials for biological recognition purposes [1, 2]. The quality of the SAM adsorption on the electrode surfaces will play an important role in affecting the sensing performance of these electrodes. In this work, we present electrochemistry-based voltammetric oxide-reduction and adsorption-stripping methods to characterize the adsorption of two SAM alkanethiols on substrates made of arrays of skyscraper nanopillars.

Materials and Methods: Two alkanethiol SAMs, 3-mercaptopropionic acid (MPA: $HS-(CH_2)_2-COOH$) and 11-mercaptoundecanoic acid (MUA: $HS-(CH_2)_{10}-COOH$) from Sigma (St. Louis, MO) were used. 3D electrodes made of arrays of skyscraper Au nanopillars were fabricated using the published method [1, 2]. For SAM formation, the 3D electrodes were placed in ethanol solution containing 10 mM of either MPA or MUA for 24 hours followed by washing in ethanol. To characterize the SAM adsorption, electrochemical cyclic voltammetry (CV) was performed at 25°C in a three-electrode cell with a platinum (Pt) counter electrode and an Ag/AgCl reference electrode using a potentiostat (Solartron 1480, Houston, TX). First, CV for reducing the Au-oxide was performed in 0.1 M H_2SO_4 from -0.5 V to 1.5 V at 100 mV/s and the percent defect in the SAMs was evaluated from the reduction peak current associated with the exposed Au-oxide. Then CV for stripping the SAM adsorption was performed in 0.1 M NaOH from -1.6 V to -0.2 V at 100 mV/s and the SAM surface coverage (Γ) was determined by $\Gamma=Q/nFA$ [3], where Q is the amount of charge passed for SAM stripping (determined from the reduction peak current associated with alkanethiol desorption), n is the number of electrons involved in the stripping reaction (n=1), F is the Faraday constant (96485 C/mol) and A is the electroactive surface area (0.04 cm^2).

Results: Fig.1A shows the CV curves for the reduction of the exposed Au-oxide. All these CV curves exhibit an Au-oxide reduction peak at around 0.78 V, indicating that all these 3D electrodes possess a certain amount of defects in the SAMs covering the electrode surfaces. By the ratio of the area under the reduction peak (by integrating the CV curve under the peak) of the SAM treated 3D electrodes to that of a bare 3D electrode, a measure of percent defect in these SAMs was obtained: the percent defect is approximately 87.3% and 37.8% for the MPA and MUA SAMs, respectively. These values are high when compared with flat electrodes: 52% for the MPA and 0% for the MUA SAMs [4], as expected due to the presence of the closely packed skyscraper nanopillars. Fig.1B shows the CV curves for the stripping of the adsorbed

SAMs. Two peak currents are visible in the CV curves for both MPA and MUA. We reckoned that the peak at -0.82 V for MPA and -1.03 V for MUA is due to the cleavage of the Au-sulfur bond, based on the literature results of a desorption peak within -0.6 and -0.9 V for short alkanethiols (n=2 to 6) and -1.0 and -1.2 V for long alkanethiols (n=11 to 18). The Γ values are found to be 1.38×10^{-8} mol/cm^2 for MPA and 2.37×10^{-8} mol/cm^2 for MUA, which are about 27 to 28 times higher than those for MPA (5.12×10^{-10} mol/cm^2) and MUA (8.30×10^{-10} mol/cm^2) on flat surfaces [4], owing to the presence of these skyscraper nanopillars in these 3D electrodes.
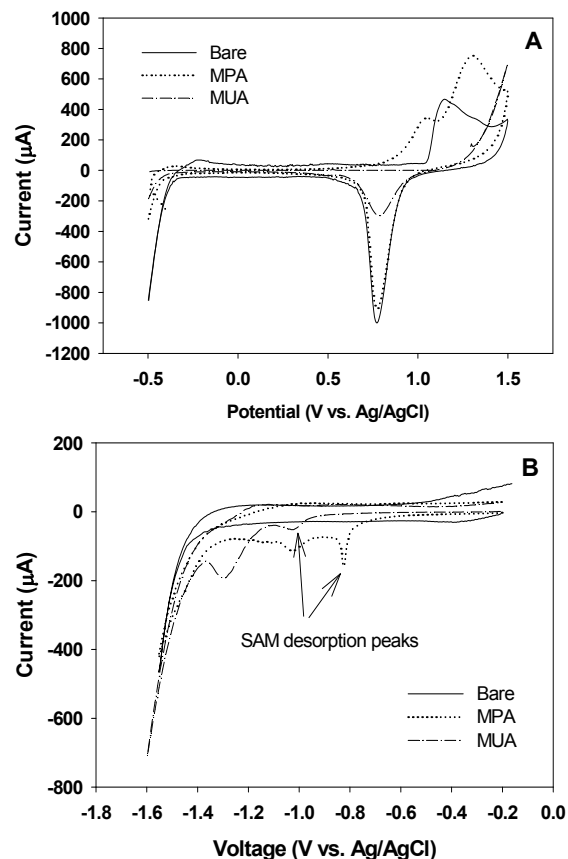

Fig.1 – CV curves for the reduction of Au-oxide in 0.1 M H_2SO_4 (A) and for the stripping of adsorbed SAMs 0.1 M NaOH (B).

Conclusions: The voltammetric oxide-reduction and adsorption-stripping methods are proven effective in characterizing the adsorption of alkanethiol SAMs on 3D electrodes made of skyscraper nanopillars. On these 3D electrodes, MUA exhibits a larger surface coverage with less percent defect than MPA.

References: Zhang G. et al., 2008. Biosensors and Bioelectronics 23(7), 1117-1124.
Zhang G. et al., 2008. Nanotechnology 19, 395501.
Porter MD. et al., 1991. Langmuir 7(11), 2687-2693.
Campuzano S. et al., 2002. J Electro Chem 526, 92-100.