Porphyrin-Based Molecular Multilayer Films Assembled via Cu(I)-Azide-Alkyne Cycloaddition Coupled Layer-by-Layer Method for Light Harvesting Applications

by

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An Abstract of a Thesis Submitted to the Graduate

Faculty of Rensselaer Polytechnic Institute

in Partial Fulfillment of the

Requirements for the degree of

DOCTOR OF PHILOSOPHY

Major Subject: Chemistry

The original of the complete thesis is on file
In the Rensselaer Polytechnic Institute Library

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July 2012
(For Graduation August 2012)

ABSTRACT

We have developed a Layer-by-Layer (LbL) method for the fabrication of thin-film molecular multilayers on electron-beam evaporated Au surfaces. Copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) coupling reactions were used for initial surface attachment and subsequent LbL deposition. The molecular multilayer films comprised of porphyrins and multi–azido linkers were assembled and characterized with a multitude of surface techniques. The electrochemical and photophysical properties of the thin-films can be tuned through synthetic modification of the individual building blocks, resulting in new porphyrin multilayers. These films have applications as light-harvesting arrays in Dye-Sensitized Solar Cells (DSSC), molecular electronics, and sensors.

Herein, we demonstrate the reproducible growth trends and optical properties of multilayer films on Au surfaces modified with an azido–terminated alkanethiol self-assembled monolayer. Multilayer growth was followed by UV-Vis absorption and specular reflectance spectroscopy. Film thickness and optical constants were obtained through spectroscopic ellipsometry. The resulting extinction coefficients were consistent with typical porphyrin absorption spectra. The multilayers show consistent linear growth in absorbance and film thickness over tens of layers as well as continuity and moderate ordering in their molecular structure. This flexible molecular LbL technique has the potential to control the nanoscale structure and function of the thin films. Topology and local surface roughness were examined by TM-AFM, and elemental composition found by X-ray Photoelectron Spectroscopy (XPS) was consistent with the expected morphology of the porphyrin based films assembled on Au surfaces. Additionally, the copper content of the resulting films was quantified by XPS, and the utility of ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) was examined to remove the adventitious Cu catalyst. The gold supported multilayers were developed as a test-bed of the films' electrochemical properties were studied by cyclic voltammetry and interfacial electron transfer rate constants were measured using chronoamperometry. It is crucial to examine the electron transport in the films in order to determine the applicability of the films for DSSC.

Additionally, films grown on silicon oxide surfaces were also characterized in a similar manner as those on gold. Specular X-ray Reflectivity (XRR) measurements were done for silicon oxide supported films, and yield an average thickness of the films and confirm highly linear dependence of the film thickness on bilayer number. Macroscopic surface roughness was determined by XRR and data fitting. It was found to increase with the number of layers and generally was around 12% of the film thickness for silicon oxide supported films. Tapping mode AFM measurements confirm the continuous nature of the thin films and the local roughness, which had values slightly larger than those determined from XRR. Spectroscopic ellipsometry analysis yielded film thickness and optical constants. The film thickness correlated well with XRR derived film thickness, although it was slightly higher. The average molecular growth angles were estimated by comparing intramolecular distances from DFT modeling with experimental film thicknesses and found to be between 40° and 70° with respect to the substrate surface, depending on the bonding configuration.

The above described results confirm that the porphyrin-based multilayers can be reproducibly grown using the LbL method and CuAAC interlayer coupling on various substrates and potentially become a new class of light harvesting arrays for DSSC, molecular electronics, and sensors.