Electrochemistry Using Self-Assembled DNA Monolayers on Highly Oriented Pyrolytic Graphite

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Abstract:

Duplex DNA functionalized with pyrene has been utilized to fabricate DNA-modified electrodes on highly oriented pyrolytic graphite (HOPG). Films have been characterized using AFM and radioactive labeling as well as electrochemically. The data obtained are consistent with a close-packed structure in the film with helices oriented in a nearly upright orientation, as seen earlier with the fabrication of thiol-tethered duplexes on gold. Also as on gold, we observe the reduction of DNA-bound intercalators in a DNA-mediated reaction. The reduction of the intercalator is attenuated in the presence of the single-base mismatches, CA and GT, independent of the sequence composition of the oligonucleotide. This sensitivity to single-base mismatches is enhanced when methylene blue reduction is coupled in an electrocatalytic cycle with ferricyanide. The extended potential range afforded by the HOPG surface has allowed us also to investigate the electrochemistry of previously inaccessible metallointercalators, $Ru(bpy)_2dppz^{2+}$ and $Os(phen)_2dppz^{2+}$, at the DNA-modified HOPG surface. These results support the application of DNA-modified HOPG as a convenient and reproducible surface for electrochemical DNA sensors using DNA-mediated charge transport.