Experimental report

05/01/2022

Proposal: **9-13-883** **Council:** 10/2019

Title: Effects of a redox polymer on the interactions between the protein cytochrome c and conductive carbon surfaces.

Research area: Chemistry

This proposal is a new proposal

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Local contacts: Samantha MICCIULLA

Samples: Cytochrome C
Carbon/silicon
Osmium redox polymer

Instrument	Requested days	Allocated days	From	To
D17	2	2	16/03/2021	18/03/2021

Abstract:

This proposal builds on a previous successful experiment studying the structural changes of an electron-transfer protein, cytochrome c, under electrochemical control. Here, we wish to extend this project to look at its behaviour on carbon surfaces and study the effects of a redox polymer that is believed to enhance conductivity between the protein and surface.

Experimental report: 9-13-883: Conductive polymers

Background

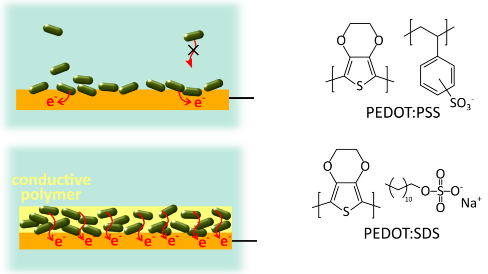

Figure 1: Schematic showing effects of a conductive polymer to immobilise cyanobacteria onto the electrode (LHS) and structures of the two PEDOT/dopant combinations used in this work (RHS).

In this experiment, we aimed to investigate the structure of a conductive polymer—PEDOT—at the electrode/electrolyte interface as a function of applied potential. This polymer is currently being investigated for its potential use in biophotovoltaic (BPV) technology, in which biofilms of photosynthetic bacteria are grown onto electrodes and used to harvest solar energy. Such devices remain surprisingly inefficient, however, with inexplicably slow electron-transfer at the bacteria/electrode interface. By using conductive polymers such as PEDOT, the hope is to improve both adhesion of bacteria to the electrode and electron transfer efficiency (Figure 1). However, previous work has indicated there may be some form of structural changes in the PEDOT layers after prolonged periods at an applied potential, with SEM images suggesting either some swelling behaviour and/or deposition of a surface-based salt film.

Results

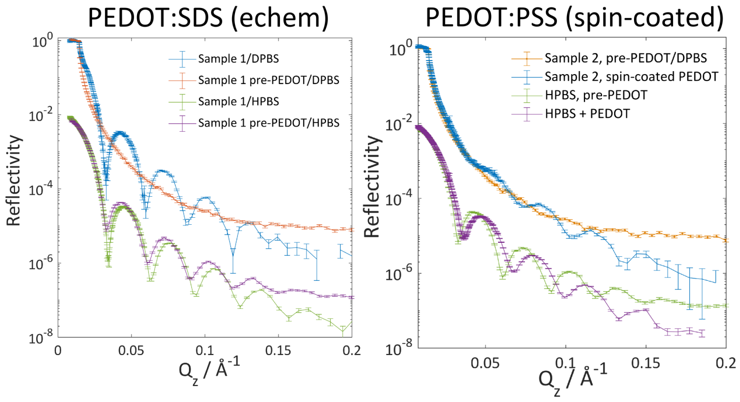

Figure 2: Raw NR data comparing the electrochemically-grown (LHS) and spin-coated (RHS) PEDOT films on carbon. Data vertically offset for clarity.

In this work, we compared two approaches by which we attempted to form PEDOT layers appropriate for NR analysis: by electrochemically growing the films (using SDS as dopant) and by spin-coating (with PSS as dopant). Interestingly, given both films were visibly inhomogeneous by eye, they still gave rise to acceptable NR data, with the spin-coated samples being slightly rougher (Figure 2).

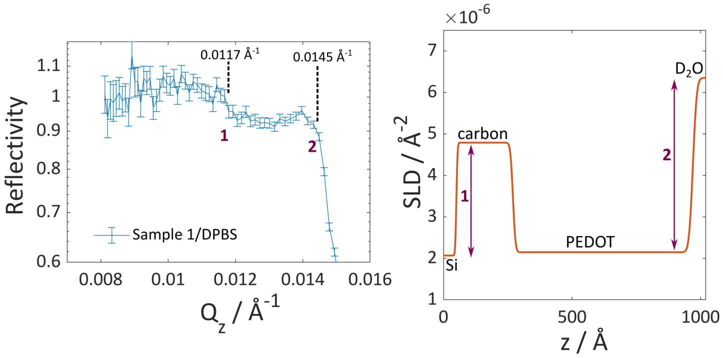

Figure 3: Close-up of the critical edge area for the electrochemically-grown PEDOT layer on carbon, with simulated SLD profile (PEDOT thickness greatly decreased for clarity).

The high thickness of the PEDOT layers gave rise to a double critical edge for both samples, which has proved both a challenge and a blessing. A key advantage has been that the position of the critical edges has allowed us to directly extract the SLDs of the carbon and PEDOT layers (Figure 3)—interestingly, the carbon SLD was found to have significantly decreased (from *ca* 7 x 10^{-6} Å^{-2} to *ca* 5 x 10^{-6} Å^{-2}) since they were used in a previous NR experiment a few months previously, suggesting that the preparation procedures used here (plasma- and nitric-acid cleaning, and applying potentials) may have somehow significantly reduced the film density.

More challenging has been the modelling of the data as currently available fitting software packages are unable to account for such thick layers (estimated to be around 500-1000 nm based on spin-coating thickness calculations). We have therefore been developing a custom-made python-based code to model the data. Although this is still ongoing, it has usefully shown that the main Kiessig fringes are essentially unaltered by changes in the PEDOT fringes, and so we have concentrated our analyses entirely on the critical edge region.

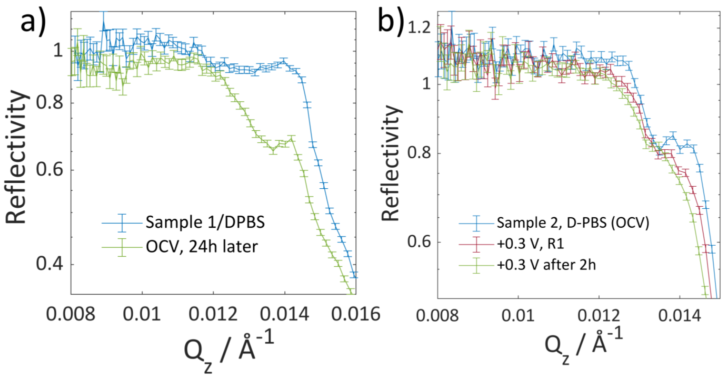

Figure 4: Critical edge region for a) sample 1 (electrochemically-grown PEDOT) and b) sample 2 (spin-coated PEDOT).

Some examples of the data are shown in Figure 4. Interestingly, the two samples (prepared differently) showed different behaviour; the electrochemically-grown PEDOT greatly increased in thickness and roughness, and reduced in SLD (and therefore density), when soaked in the buffer solution, suggesting it had swollen in the solvent (Figure 4a), whereas the spin-coated sample, which was initially thicker, showed a significant roughening when initially soaked in solution (Figure 4b) although the sharpness of the critical edges was subsequently regained after a negative potential had been applied. Our analysis is still ongoing, but it seems that this critical edge region is highly informative in monitoring the structural changes for these thick polymer samples.