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Immobilization of Pyrroloquinoline Quinone on Few-Walled Carbon Nanotubes

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Introduction

Pyrroloquinoline quinone (PQQ) is an important biomolecule. It is one of the cofactors in quinoproteins, which are enzymes catalyzing the oxidation of many organic molecules, like alcohols, sugars and primary amines. Examples of such enzymes are alcohol and glucose dehydrogenase (EC 1.1.98.8 and 1.1.98.2). In these enzymes, PQQ is tightly bound, which makes them attractive for simple biosensors as the cofactor does not need to be present in the bulk solution. Furthermore, PQQ-dependent enzymes do not require oxygen as the electron acceptor making them applicable to non-oxygenous environments. These enzymes have been used for example as biosensor candidates for glucose and alcohol detection [1]. PQQ itself can also catalyze the oxidation of these substrates and of another common cofactor, nicotinamide adenine dinucleotide (NAD), which exhibits very irreversible electrochemistry. Therefore, the electrochemistry of PQQ is very important for biosensor and biocatalysis research.

For a reversible redox reaction usually a modified electrode is used or PQQ is immobilized on the electrode [2]. Here we present a simple immobilization strategy employing few-walled carbon nanotubes and explore its pH dependence.

This study was also published in Electrochemistry Communications 12 (2010) 1257.

Experimental

Few-walled carbon nanotubes (FWCNT, <10 nm diam.) were synthesized by chemical vapour deposition of methane catalyzed by Co and Mo. Vulcan XC72R and single-walled carbon nanotubes were purchased from Cabot Corporation and Cheap Tubes, respectively. A modified glassy-carbon disk electrode was prepared by dropping an aliquot of the carbon material in 2-propanol on the electrode and letting it dry in ambient conditions. The electrode was then saturated with PQQ by dipping it in buffered PQQ solution for 2 hours.

Electrochemical characterization of the electrodes was carried out in a three-electrode cell. PQQ electrode was the working electrode, platinum wire the counter electrode and saturated calomel electrode the reference electrode. Supporting electrolyte was 0.2 M phosphate buffer at various pH values and measurements were made under nitrogen atmosphere.

Results

Few-walled carbon nanotubes show excellent adsorption properties:

30 times more PQQ on FWCNTs than on carbon black (Vulcan) or commercial SWCNTs

The electrochemical response of the electrode is strong and reversible in a wide pH window: highest reversibility and stability in low pH

The adsorption can be controlled by the solution pH: dipping in basic pH results in decreased absorption due to increased electrostatic interference (both PQQ and FWCNTs negatively charged)

References
1. V. Laurimavicus et al., Bioelectrochemistry 55 (2002) 29

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