

# Critical assessment of the Quartz Crystal Microbalance with Dissipation as an analytical tool for biosensor development and fundamental studies: Metallophthalocyanine–glucose oxidase biocomposite sensors

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## Abstract

One of the challenges in electrochemical biosensor design is gaining a fundamental knowledge of the processes underlying immobilisation of the molecules onto the electrode surface. This is of particular importance in biocomposite sensors where concerns have arisen as to the nature of the interaction between the biological and synthetic molecules immobilised. We examined the use of the Quartz Crystal Microbalance with Dissipation (QCM-D) as a tool for fundamental analyses of a model sensor constructed by the immobilisation of cobalt(II) phthalocyanine (TCACoPc) and glucose oxidase (GOx) onto a gold-quartz electrode (electrode surface) for the enhanced detection of glucose. The model sensor was constructed in aqueous phase and covalently linked the gold surface to the TCACoPc, and the TCACoPc to the GOx, using the QCM-D. The aqueous metallophthalocyanine (MPc) formed a multi-layer over the surface of the electrode, which could be removed to leave a monolayer with a mass loading that compared favourably to the theoretical value expected. Analysis of frequency and dissipation plots indicated covalent attachment of glucose oxidase onto the metallophthalocyanine layer. The amount of GOx bound using the model system compared favourably to calculations derived from the maximal amperometric functioning of the electrochemical sensor (examined in previously-published literature, Mashazi, P.N., Ozoemena, K.I., Nyokong, T., 2006. *Electrochim. Acta* 52, 177–186), but not to theoretical values derived from dimensions of GOx as established by crystallography. The strength of the binding of the GOx film with the TCACoPc layer was tested by using 2% SDS as a denaturant/surfactant, and the GOx film was not found to be significantly affected by exposure to this. This paper thus showed that QCM-D can be used in order to model essential processes and interactions that dictate the functional parameters of a biosensor.

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## 1. Introduction

The Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) is a piezoelectric sensor that is frequently used to monitor molecule interaction on the surface of a piezoelectric sensor platform. Previous research using this analytical technique has focused on such diverse elements of research as: bio-photovoltaic cell construction (Lam et al., 2006), protein–surface interactions (Höök and Kasemo, 2001; Andersson et al., 2004; Hemmersam et al., 2005), antibody–antigen interactions (Marx et al., 2007; Larsson et al.,

2005), protein–protein interactions (Limson et al., 2004) and cell adhesion monitoring for implant surface technology (Lord et al., 2006; Modin et al., 2006).

Data retrieved from QCM-D analysis is two-fold. Firstly, the frequency shift ( $\Delta f$ ) upon attachment/detachment of electrode-bound mass is related to the mass by the Sauerbrey equation (Eq. (1)):

$$\Delta m = \frac{\Delta f \times C}{n} \quad (1)$$

where  $\Delta f$  is the frequency shift (in Hz),  $\Delta m$  the mass area change (in  $\text{ng cm}^{-2}$ ),  $C$  the mass sensitivity ( $17.7 \text{ ng cm}^{-2} \text{ Hz}^{-1}$  at an oscillation frequency of 5 MHz, or overtone  $n = 1$ ) and  $n$  is the overtone number (1, 3, 5, 7 ...). The Sauerbrey equation may also be used to estimate the layer thickness and viscosity of the

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