Quantum dot electrode for light-controlled biosensors

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Abstract
This study examines the oxygen dependency of the photocurrent of gold electrodes, which are modified with quantum dots (CdSe/ZnS nanoparticles). The oxygen dependent photocurrent is affected by the polarization of the electrode and the pH-value. In addition it is shown that an electrode modified with quantum dots also allows the detection of an enzyme reaction in solution. Based on this a photo-bio-electrochemical sensor for glucose detection is developed. The sensor can be read out by illumination the responding element area and photocurrent detection.

Key words: photocurrent, quantum dots, enzyme, electrochemical sensor, nanoparticles

Introduction
As already known, based on the charge carrier generation during illumination, quantum dots (QD) allow the generation of a photocurrent, when they immobilized on electrodes. This photocurrent depends on the applied potential and can be specifically influenced by analyte concentrations [1-3]. Therefore, different reactions on a non-structured electrode surfaces by photo exciting the respective electrode area can be read out. Here we investigate how the oxygen sensitivity of quantum dot electrodes can be exploited for sensorial applications.

Results
Gold electrodes are modified with CdSe/ZnS quantum dots by means of a dithiol. With these electrodes it is found, that basic or neutral pH-values and potentials below -300mV (vs. Ag/AgCl) are favorable for a pronounced catodic photocurrent. This can be attributed to oxygen reduction.

Fig. 1. Schematic diagram of the light-switchable electrode with glucose oxidase and its electron transfer steps.

Due to the catalytic reaction of an oxidase, the oxygen dependent photocurrent can be suppressed. This is demonstrated with glucose oxidase (GOD); activities down to 0.025 U/mL can be measured in solution. Furthermore, GOD is immobilized on a quantum dot electrode with two different strategies, aimed at a very high molecular density of the enzyme. One method uses chemical crosslinking with a bifunctional reagent. It can be shown that the photocurrent change is a defined function of glucose concentration (see Fig.3).

Fig. 2. Neutral/basic pH-value is favourable for high O₂-sensitive photocurrent (Photocurrent difference between air- and argon purged buffer)
Fig. 3. Suppression of the photocurrent of Au-[QD-BDT]-GOD electrodes with a cross-linked GOD-network prepared with different enzyme concentrations in dependence on glucose concentration. The different curves illustrate the sensing behavior of electrode prepared with increasing GOD concentrations: (I) 200 µM GOD; (II) 400 µM GOD; (III) 2mM GOD (100 mM HEPES; pH 6.8; tlight = 10s; E = -350 mV vs. Ag/AgCl, 1 M KCl). BDT = benzene dithiol

Another strategy uses the layer-by-layer assembling of GOD and poly-(allylamine hydrochloride) (PAH). Mass-sensitive analysis with QCM (quartz crystal microbalance) proves successful layer formation [GOD/PAH]n, which is largely due to electrostatic interactions. Photocurrent measurements show an increased sensitivity for glucose with increasing number of GOD layers (see Fig.4). Glucose can be sensitively measured in the range of 100 µM up to 5 mM. The principle is also applicable to other enzymes, providing access to multiple analysis on a single sensor chip.

Fig. 4 Relative suppression of the photocurrent of an Au-[QD-BDT] electrode increases with the number of immobilised [GOD/PAH]n-layers. (a) 2 layer, (b) 4 layer, (c) 6 layer (100 mM HEPES pH 6.8; tlight = 10s; E = -350 mV vs. Ag/AgCl, 1 M KCl).

References


Acknowledgment

This work was partially supported by the DFG (project LI706/2-1).