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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.

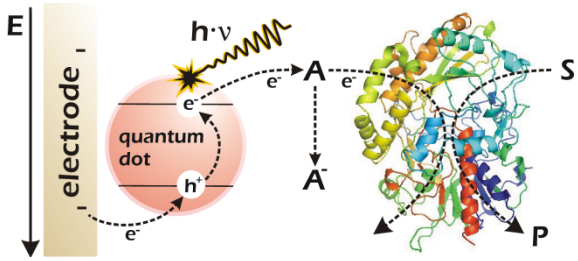

Fig. 1. Schematic diagram of the light-switchable electrode with glucose oxidase and its electron transfer steps.

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.

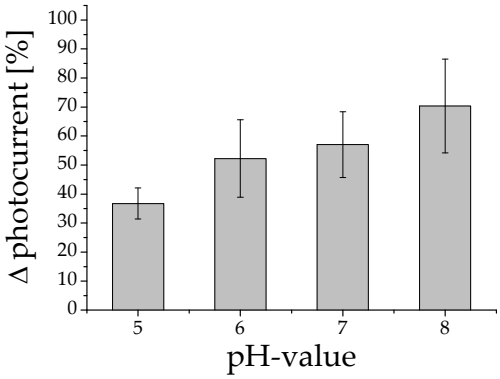

Fig. 2. Neutral/basic pH-value is favourable for high O_2 -sensitive photocurrent (Photocurrent difference between air- and argon purged buffer)

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).

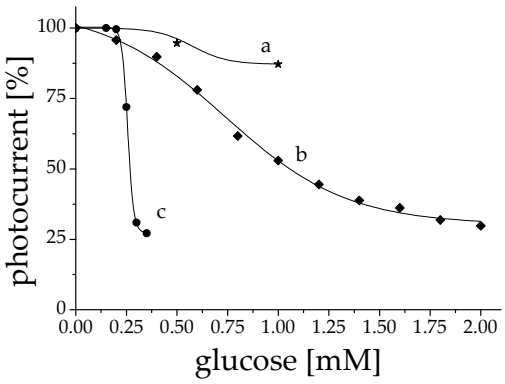

Fig. 3. *Suppression of the photocurrent of Au-[QD-BDT]-GOD electrodes with a cross-linked GOD-network prepared with different enzyme concentrations in dependence on glucose concentration. The different curves illustrate the sensing behavior of electrode prepared with increasing GOD concentrations: (I) 200µM GOD; (II) 400µM GOD; (III) 2mM GOD (100mM HEPES; pH 6.8; t_{ligth}= 10s; E= -350mV vs. Ag/AgCl, 1M KCl). BDT= benzene dithiol*

Another strategy uses the layer-by-layer assembling of GOD and poly-(allylamine hydrochloride) (PAH). Mass-sensitive analysis with QCM (quarz cristal microbalance) proves successful layer formation $[GOD/PAH]_x$ 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.

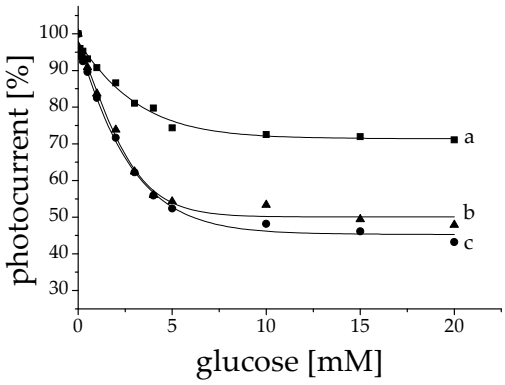

Fig. 4 Relative suppression of the photocurrent of an Au-[QD-BDT] elctrode increases with the number of immobilised $[GOD/PAH]_n$-layers. (a) 2 layer, (b) 4 layer, (c) 6 layer (100mM HEPES pH 6.8; t_{ligth}= 10s; E= -350mV vs. Ag/AgCl, 1M KCl)

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