Photobioelectrochemical sensors based on the combination of quantum dot electrodes with enzyme reactions

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Quantum dots, immobilized on electrodes, allow the generation of a photocurrent which is dependent on the applied potential and thus, can work as a light-switchable layer on the sensor surface. The quantum dots can not only interact with the electrode upon illumination but can also exchange electrons with reaction partners in solution allowing the construction of signal chains starting from analyte molecules to be detected [1; 2].

In this work the oxygen dependence of the photocurrent of gold electrodes modified with CdSe/ZnS-quantum dots has been studied. QD immobilisation on the electrode is achieved using a dithiol compound. It has been found that the cathodic photocurrent is enhanced in the presence of oxygen; the current is also influenced by the polarization of the electrode (-500 to +100mV vs Ag/AgCl) and the pH of the solution. It can be also shown that the photocurrent follows the absorption properties of the immobilized QD.

The QD-modified electrode can be used to detect enzyme reactions in solution, this can be shown with lactate dehydrogenase and glucose dehydrogenase [2-4] allowing the analysis of the respective substrate. Here we use the electrode to monitor the activity of the oxygen consuming glucose oxidase (GOD) in solution. Rather small GOD activities (0.025 U/ml) can be detected by photocurrent measurements.

In order to develop a photoelectrochemical biosensor, GOD is immobilized on top of the CdSe/ZnS-electrode. Two different approaches have been followed. The first method is based on the covalent cross-linking of GOD with a bifunctional agent. It can be shown that the consumption of oxygen near the QD surface is a function of the concentration of glucose. The second immobilization strategy uses the layer-by-layer-technique to assemble GOD and poly(allylamin hydrochloride) (PAH). Mass sensitive analysis proves the assembly of $[GOD/PAH]_n$-layer systems (n=2,4,6) on the surface. Photocurrent measurements demonstrate an increased glucose sensitivity with an increase in the number of GOD layers. High enzyme concentrations results in a well detectable photocurrent change between 100µM and 5mM glucose ($[GOD/PAH]_4$-layer-QD-electrode). This allows substrate detection by illumination of the respective sensor surface and thus provides the basis for a spatial read out of the sensing electrode.

References:

[1] C. Stoll, S. Kudera, W. Parak, F. Lisdat, Small 2(6) (2006) 741.
[2] E. Katz, M. Zayats, I. Willner, F. Lisdat, Chem. Comm. 13 (2006) 1395.
[3] C. Stoll, C. Gehring, K. Schubert, M. Zanella, W. Parak, F. Lisdat *Biosens. & Bioelec.* 24 (2008) 260.
[4] K. Schubert, W. Khalid, Z. Yue, W. J. Parak, F. Lisdat *Langmuir* 26(2) (2010) 1395.