Electrochemical Bioassays Based on Modulated Growth of Quantum Dots

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We pioneered bioassays in which analytes modulate the formation of CdS quantum dots (QDs) *in situ*. Our early assays were applied to fluorogenic determination of enzymatic activities of enzymes such as acetylcholine esterase[1], horseradish peroxidase[2], glucose oxidase[3] etc. We report a new class of sensitive electrochemical assays employing generation *in situ* of QDs suitable for determination of analytes using affinity interaction and oxidative properties of metal cations. In our new immunno assay alkaline phosphatase conjugated to antibody calalyzes formation of CdS QDs[4]. Irradiation of QDs with the standard laboratory UV-illuminator results in photooxidationof 1-thioglycerol (TG) mediated by Os–PVP complex on the surface of graphite electrode at appliedpotential of 0.31 V vs. Ag/AgCl. (Figure 1). We, also, designed a new assay based on microbead linked enzymatic generation of CdS QDs (Microbead QD-ELISA)[5]. The resulting QDs were detected by fluorescence spectroscopy, microscopy, and square-wave voltammetry (Figure 2). We discovered that cysteine (CSH) readily stabilizes CdS QDs growing in aqueous solutions. Oxidation of CSH by hydrogen peroxide (H_2O_2) at room temperature yields cystine (CSSC) which does not stabilize CdS QDs so efficiently as CSH does. Such oxidation causes the decrease in the rate of the formation of CSH-capped CdS. For the first time, we combined the oxidation of CSH with copper ions or biocatalytic oxidation of D-glucose catalyzed by glucose oxidase[6] (Figure 3). Electrochemical detection strategies employing semiconductor growth of CdS quantum dots (QDs) *in situ* open up new opportunities for highly sensitive detection of biological targets.

References

[1] L. Saa, A. Virel, J. Sanchez-Lopez,V. Pavlov, Chem. Eur. J. 16 (2010) 6187
[2] R. Grinyte, L. Saa, G. Garai-Ibabe, V. Pavlov, Chem. Commun. 51 (2015) 17152
[3] L. Saa, V. Pavlov, Small, 8 (2012) 3449
[4] J. Barroso, L. Saa, R. Grinyte, V. Pavlov, Biosens. Bioelectron. 77(2016) 323
[5] R. Grinyte, J. Barroso, M. , L. Saa, V. Pavlov, ACS Appl. Mater. Interfaces, 8(2016) 29252
[6] R. Grinyte, J. Barroso, L. Saa, V. Pavlov, Nano Res. 2016, DOI:10.1007/s12274-016-1378-1

Figure 1: Immunoassay using photoelectrochemical detection of enzymatically generated CdS QDs

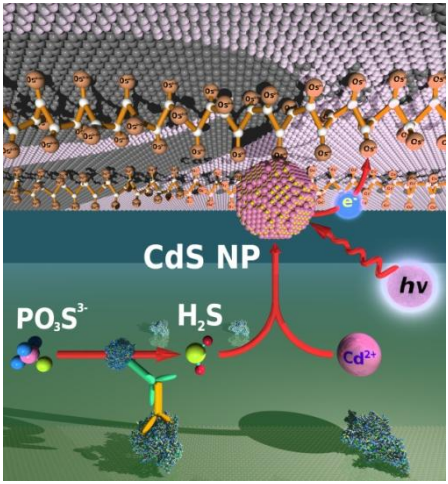

Figure 2: Microbead ELISA using biocatalytic formation of QDs for ultra high sensitive electrochemical detection

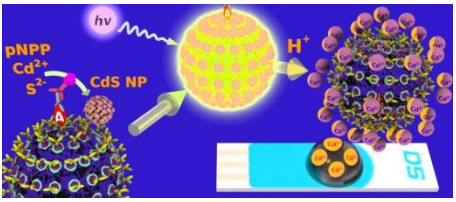

Figure 3: Photoelectrochemical assay for copper and glucose using modulation of growth of Cysteine-capped QDs