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, horseradish peroxidase, glucose oxidase 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 immuno assay alkaline phosphatase conjugated to antibody catalyzes formation of CdS QDs. Irradiation of QDs with the standard laboratory UV-illuminator results in photooxidation of 1-thioglycerol (TG) mediated by Os–PVP complex on the surface of graphite electrode at applied potential 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). 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 (H2O2) 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 (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


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