Optical and Electrochemical Bioassays Using Photocatalytic Activity of Semiconductor Quantum Dots

Valery Pavlov
Javier Barroso, Laura Saa, Blatriz Diez
CIC BiomaGUNE, Paseo Miramon, San Sebastian, Spain
vpavlov@cicbiomagune.es

Nanomaterials based analytical assays are becoming a promising low cost approach for the detection of analytes. Usually, nanomaterials like metal and semiconductor nanoparticles (SNPs) were employed in analytical systems as fluorescent and electrochemical labels tethered to recognition elements such as antibodies and DNA oligomers, enhancers of raman scattering, fluorescence quenchers or tracers. Moreover, metal nanoparticles (NPs) can be generated in situ in the course of biocatalytic processes catalyzed by different enzymes. Unfortunately, metal NPs produced in situ in the above mentioned biocatalytical assays are not fluorescent thus the sensitivity of those assays is limited by the sensitivity of UV-Vis spectroscopy employed to follow the formation of gold and silver NPs. SNPs used in biochemical assays are fluorescent and demonstrate quantum effects. They emit photons of light upon photoexcitation hence they are referred to as quantum dots (QDs). QDs allow to use much more sensitive fluorescence spectroscopy and photoelectrochemistry to follow the readout signal. We pioneered bioassays in which analytes modulate the formation of CdS 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 reported 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. Os–PVP complex mediated the electron transfer between the electrode surface and CdS NPs. We proved that our assay covers the European Union standard limit of Cu2+ ions in drinking water.

We discovered that copper ions (Cu2+) catalyze the oxidation of CSH by oxygen (O2) to modulate the growth of CSH-capped CdS QDs. This new chemical process was applied to sensitive fluorogenic and photoelectrochemical (PEC) detection of Cu2+ ions in real samples of mineral and tap water using the photocatalytic activity of the resulting NPs. Disposable screen-printed electrodes (SPCEs) modified with electroactive polyvinylpyridine bearing osmium complex (Os-PVP) by cyclic voltammetry (CV) were employed for PEC analytical system. CdS NPs formed during the assay photocatalyze oxidation of 1-thioglycerol (TG) upon application of 0.3 V vs. Ag/AgCl to SPCEs. Os-PVP complex mediated the electron transfer between the electrode surface and CdS NPs. We proved that our assays did not suffer from interference from other ions accompanying Cu2+ and the sensitivity of our assays covers the European Union standard limit of Cu2+ ions in drinking water.

The other poison, methanol is frequently discovered in alcoholic beverages. We reported for the first time a new strategy for the detection of methanol using fluorescence spectroscopy and photoelectrochemical (PEC) analysis. The analytical system is based on the oxidation of CSH with hydrogen peroxide enzymatically generated by alcohol oxidase (AOX). H2O2 oxidizes capping agent CSH, modulating the growth of CSH-stabilized CdS QDs. Disposable screen-printed carbon electrodes (SPCEs) modified with a conductive osmium...
polymer (Os-PVP) complex were employed to quantify resulting CdS QDs. This polymer facilitates the “wiring” of in situ enzymatically generated CdS QDs, which photocatalyze oxidation of 1-thioglycerol (TG), generating photocurrent as the readout signal. Likewise, we proved that our systems did not suffer from interference by ethanol. The PEC assays showed better sensitivity than conventional methods, covering a wide range of potential applications for methanol quantification.

Optical and electrochemical detection strategies employing semiconductor growth of CdS QDs in situ open up new opportunities for highly sensitive and selective determination of target analytes.

References


Figures

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. Fluorometric assay for glucose oxidase activity.

Figure 4. Photo-electrochemical bioassay for methanol.