Enzymatic etching of nonoparticles in biosensing

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Abstract
The physical properties of inorganic nanoparticles (NPs) depend on their shape, size and composition. Noble metal NPs exhibit strong localized surface plasmon resonances (LSPR) in the visible or near-IR wavelength range. Hence, metal and semiconductor NPs of different nature have found broad application in imaging and colorimetric bioanalytical assays. Gold nanorods (AuNRs) and fluorescent semiconductor quantum dots (QDs) can be employed as a highly sensitive platform to probe environmental changes through variations in their size. The longitudinal LSPR frequency demonstrated by Au NRs is highly sensitive to minute changes in the AuNR aspect ratio. The emission spectra of spherical QDs depends on their diameter and concentration. We discovered for the first time that the oxidative enzyme Horseradish Peroxidase is able to produce free radicals which oxidize AuNRs and semiconductor QDs. We introduced novel bio-analytical assays based on enzymatic etching of inorganic nanoparticles. HRP is able to induce a gradual oxidation of the AuNRs in the presence of trace concentrations of H_2O_2 and halide ions.[1] As a consequence, other enzymatic reactions, carried out by Glucose Oxidase (GOx) can be easily coupled to the HRP activity assay, thereby allowing for the detection of different amounts of glucose.

Modification of AuNRs with thiol-containing organic molecules such as glutathione and thiocholine hinders enzymatic etching of AuNR. Higher concentrations of thiol-containing molecules in the reaction mixture gradually decrease the rate of enzymatic etching. Interestingly, the decrease in the rate of AuNR shortening can be easily monitored by UV-Vis spectroscopy, through changes in the longitudinal LSPR band, highly sensitive to variations in AuNR aspect ratio. This effect can be applied to develop the novel optical assays for acetylcholine esterase (AChE) activity (Figure 1). The biocatalytic hydrolysis of acetylthiocholine by AChE yields thiocholine, which prevents enzymatic AuNR etching in the presence of HRP.[2]

We also descovered a facile, mild and inexpensive enzymatic etching method for resizing of CdS QDs. It was found out that the biocatalytic process involving bromide, HRP and H_2O_2 decreased the size of semiconductor CdS QDs. Thus, this phenomenon can be applied to resizing of semiconductor CdS QDs under mild physiological conditions and rapid and sensitive detection of H_2O_2 and HRP (Figure 2). It was proven that CdS QDs immobilized on polyvinyl chloride microspheres can be etched biocatalytically too. Thus, we introduced a new platform for optical detection of analytes based on etching of semiconductor NPs.[3]

References
[1] Saa L, Coronado-Puchau M, Pavlov V, Liz-Marzán LM, Nanoscale. **6(13)** (2014) 7405.
[2] Saa L, Grinyte L, Liz-Marzán LM, Pavlov V. manuscript in preparation.
[3]] Grinyte R, Saa L, Garai-Ibabe G, Pavlov V, Chem. Commun., **51**, (2015),17152.

Figures

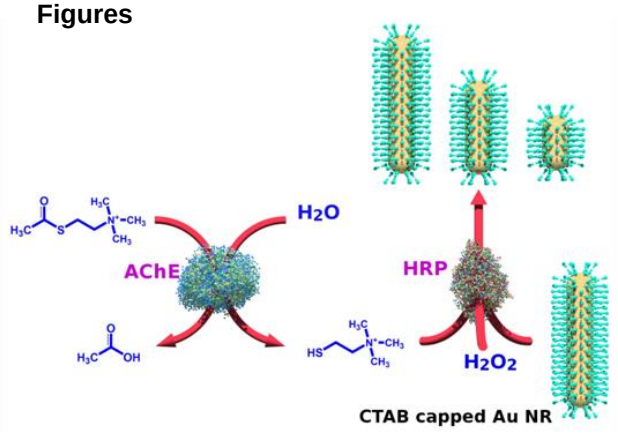

Figure 1. Protective effect of thiol molecules (R-SH) against biocatalytic oxidative etching of AuNRs

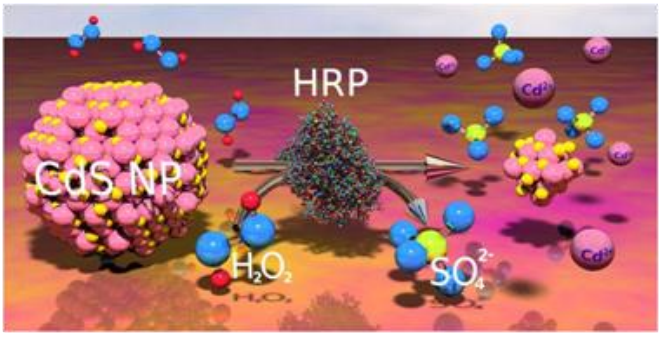

Figure 2. Enzymatic etching of CdS QDs.