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Covalent attachment of thionine onto gold electrode modified with cadmium sulfide nanoparticles: Improvement of electrocatalytic and photelectrocatalytic reduction of hydrogen peroxide

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ABSTRACT

A newly developed strategy based on gold (Au) electrode modified with cadmium sulfide nanoparticles (CdSnp) and thionine (Th) was proposed toward electrocatalytic and photoelectrocatalytic hydrogen peroxide (H_2O_2) reduction. At first, a thin film of CdS nanoparticles was electrodeposited onto Au electrode. Then, the CdS/Au electrode was modified with mercaptoacetic acid (MAA), which not only acts as a stabilizing agent to prevent the chalcogenide CdS nanocrystals from aggregation but also as a linker for subsequent attachment of Th onto the CdS nanoparticles. The effective covalent immobilization of Th was achieved through amide bond formation reaction between —NH_2 groups of Th and —COOH groups of MAA, using dicyclohexylcarbodiimide (DCC) as condensation agent. The Au/CdS/Th modified electrode showed a well-defined redox couple with surface confined characteristics at wide pH range (2–12). The heterogeneous electron transfer rate constant (k_s) and the surface coverage of immobilized Th on the modified electrode was obtained as $0.12\ s^{-1}$ and 4.35×10^{-9} mole cm^{-2}, respectively. The electrocatalytic activity and stability of the modified electrode toward hydrogen peroxide reduction was investigated and it was found that the Au/CdS/Th electrode illustrates excellent electrocatalytic activity toward H_2O_2 reduction at reduced overpotential. The detection limit, sensitivity and catalytic rate constant (k_{cat}) of the modified electrode toward H_2O_2 were 55 nM, 3.4 $\mu A\ \mu M^{-1}\ cm^{-2}$ and $3.75\ (\pm 0.1) \times 10^3\ M^{-1}\ s^{-1}$, respectively, at linear concentration range up to 10 mM. Upon light irradiation, about two-fold improvements were attained in sensitivity and detection limit of the modified electrode toward H_2O_2 electrocatalytic determination.

1. Introduction

Hydrogen peroxide has widely been used as universal oxidant in industrial and environmental processes, and it is also a very important intermediate in biological reactions. Furthermore, it is also used in various fields such as chemical and pharmaceutical industry, food production, sterilization and clinical, pulp and paper bleaching, liquid based fuel cells and security screening [1–6]. Therefore, the determination of H_2O_2 is practically important. In addition, H_2O_2 is the byproduct of the reactions which catalyzed by a large number of oxidase enzymes and its determination is very important in biosensing [6–10]. Immobilization of enzymes and proteins onto different electrode surfaces has been used as a novel strategy for fabrication of various electrochemical biosensors for H_2O_2 detection [11–15]. Short lifetime, enzyme denaturation, low stability and complex procedures in the fabrication process are disadvantageous of H_2O_2 biosensors. In addition, native enzymes gradually lose their biocatalytic activities after continuous measurements. Therefore, the development of enzymeless H_2O_2 sensors with low detection limit and wide concentration range is strongly desired. Due to the slow electrode kinetics and high overpotential required for redox reactions of H_2O_2, the electroanalytical detection of H_2O_2 at bare electrodes is not suited. Electron transfer mediators have been widely used for increasing the electron transfer kinetics and decreasing the required overpotential. Different compounds such as phthalocyanine complexes [16], polyoxoanions [17], iron-enriched natural zeolite [18], silver nanoparticles [19] prussian blue modified Au nanoparticles [20], iodine [21], water soluble dyes [22], micro tubular Te adsorbed on platinum electrode [23] and electroactive polymers [24] have been used as redox mediators for determination of H_2O_2.

To improve the performance of H_2O_2 sensors, effective immobilization of electron transfer mediator onto the electrode surface through a suitable method is of great significant. Sensitivity of the

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sensor depends on the mediator concentration at the electrode surface and modification process. Thionine (Th) is a phenothiazine redox dye which has been extensively used as electron transfer mediator since its formal potential (0.08–0.25 V *vs.* SCE in pH range 2–8) is close to that of most biomolecules redox potentials [25]. Different methods including electropolymerization [26], entrapment in different nanocomposites such as nickel oxide nanostructures [27], carbon nanotubes [28,29], Au nanoparticles [30], Au-SiO_2 nanocomposite [31], nano-TiO_2 [11,32] and covalent attachment [33–36] have been used for modification of electrode surfaces with Th and detection of H_2O_2. In noncovalent methods, the immobilized Th can easily diffuse from electrode surface into the bulk solution. Furthermore, most of Th-based sensors present quasireversible electrochemical behaviors and even ill-defined cyclic voltammograms with large background currents. Low sensitivity, reproducibility and stability, poor repeatability and short life time are also the other disadvantages of these sensors. In addition, combination of electron transfer mediator and enzymes for fabrication of H_2O_2 biosensors yet remains disadvantageous because they are complicated, expensive and their detection conditions are rigorous [11,26,30,34,35]. Hence, development of simple and reliable methods for fabricating modified electrodes capable of enzymeless detection of H_2O_2 using new electron transfer mediators and effective immobilization processes is still a challenge.

By using nanomaterials, some of the aforementioned problems such as instability and sensitivity might be overcome. Semiconductive nanocrystals (or quantum dots, QDs) have been extensively used in photoelectrochemistry, micro and photoelectronics, catalysis, electrooptics, imaging science, biological sensing, solar cells and nonlinear optics [37–39]. Photoexcitation of QDs results in the electron transition from the valence band to the conduction band, thus yielding electron–hole pairs. Photocatalytic electron and hole redox potentials of size quantized QDs can be tuned to achieve increased redox power of selective chemical reactions [40]. Furthermore, the electrodes modified with these nanomaterials have been used to develop photoelectrochemical devices able to establish active interfaces for photocurrent generation.

QDs coupled to the electroactive molecular and biomolecular units represent an original route for the generation of novel electrochemical and photoelectrchemical systems [41]. Electronic communications between photogenerated excitons and electrode surface produce anodic or cathodic photocurrents. The injection of the conduction band electrons to the electrode, with the concomitant transfer of electrons from a solution-solubilized electron donor produces an anodic photocurrent. In contrast, transfer of the conduction bond electrons to a solution-solubilized electron acceptor yields cathodic photocurrent [42]. Therefore, a layer of QDs between the electrode and a redox system can be used for a light-triggered readout of the electron transfer reaction with the electrode [42].Cadmium sulfide (CdS) as one of the most important QDs with a direct band gap of 2.4 eV has been widely applied [43,44]. Recently, the attachment of different redox enzymes or electroactive compounds onto the surface of QDs have been used to improve enzyme stability, electrocatalytic and photoelectrocatalytic activity, sensing and biosensing [45–56]. H_2O_2 detection based on the CdS QDs modified electrodes have been also reported [9,53,57]. However, low sensitivity, enzyme-dependent short lifetime, complication, high cost and poor detection conditions are some limitations of these CdS QDs-based H_2O_2 sensors and biosensors.

In the present study, the electrodeposition technique was used for preparation of CdS QDs nanparticles onto the Au electrode. Mercaptoacetic acid (MAA) was used as the stabilizing agent to prevent the chalcogenide CdS nanocrystals from aggregating. In addition, the carboxylic acid groups of MAA can be used for covalent attachment of Th *via* DCC (N,N-dicyclohexyl carbodiimide) as the condensation agent. The modified electrode revealed excellent electrocatalytic and photoelectrocatalytic activity toward H_2O_2 reduction at reduced overpotential. Micromolar or lower H_2O_2 concentrations can be detected with the modified electrode using hydrodynamic amperometry technique.

2. Experimental

2.1. Chemical and reagents

Th, $CdCl_2$, sodium thiosulphate, HCl, DCC (99%), MAA and dimethyl formamide (DMF) were purchased from Aldrich, Merckor Fluka and used without further purification. The phosphate buffer solutions (PBS) were prepared form H_3PO_4, KH_2PO_4 and K_2HPO_4 and pH values were adjusted with HCl and KOH solutions. Solutions were deaerated by bubbling high purity (99.99%) argon gas through them prior to the experiments. All electrochemical experiments were carried out at room temperature $25 \pm 0.1\,^{\circ}C$.

2.2. Apparatus and procedures

Electrochemical experiments were performed with a computer controlled μ-Autolab modular electrochemical system (Eco Chemie Utrecht, The Netherlands), driven with GPES software (Eco Chemie). A conventional three-electrode cell was used with a Ag/AgCl/(sat. KCl) as reference electrode, a Pt wire as counter electrode and a diskgold (modified and unmodified) as working electrode. Voltammetry on electrode coated with CdS and CdS/Th were performed in buffers free of thionine. The surface morphology of modified electrodes was observed with a Vega-Tescan scanning electron microscope (SEM). Photoelectrochemical experiments were performed with the cell irradiated by the white light from a tungsten lamp.

2.3. Electrodeposition of CdSnp onto the Au electrode

The gold electrode (2 mm diameter) was carefully polished with alumina powder (1 and 0.05 μm) on polishing cloth. The electrode was placed in ethanol and sonicated to remove adsorbed alumina particles. The electrodeposition of CdSnp was performed based on a previously reported procedure [58]. The electrodeposition bath was an aqueous solution (40 °C) containing $CdCl_2$ (0.1 M) and $Na_2S_2O_3$ (0.01 M) and pH of solution was adjusted to 2 with dilute hydrochloric acid. The potential of cathode was kept at −1.0 V *vs.* reference electrode and electrodeposition proceeded during120 s. After rinsing of the modified electrode with water, it can be used for electrochemical experiments immediately. The same procedure was carried out for modification of inidium tin oxide (ITO) electrode with CdS nanoparticles. The effective surface area of the electrode modified with CdSnp was determined as 0.11 cm^2 from cyclic voltammogram of 1 mM $K_3[Fe(CN)_6]$ in buffer solution, pH 7.

2.4. Modification of Au electrode with CdSnp and Th

The Au electrode modified with CdSnp film immersed in ethanol solution containing 0.01 M MAA for 3 h at constant temperature of 40 °C. MAA was used as the stabilizing agent to prevent the CdS from aggregating [59,60]. The resulting modified CdS/MAA modified gold electrode was rinsed with water. The MAA modified Au/CdSnp electrode was treated with DMF solution containing 0.1 M DCCfor 1 h in 40 °C and then rinsed with water. The DCC-activated MAA modified Au/CdS electrode was immersed in 0.01 M aqueous Th solution and shaken thoroughly for 1 h. The covalent attachment between the amino group of Th and carboxylic group of MAA was formed using DCC as condensation agent. The modified electrode was washed with water and stored in refrigerator (4 °C) when not in use. The