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Rhodium nanoparticle-modified screen-printed graphite electrodes for the determination of hydrogen peroxide in tea extracts in the presence of oxygen

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ABSTRACT

In this work we describe the fabrication of nanostructured electrocatalytic surfaces based on polyethyleneimine (PEI)-supported rhodium nanoparticles (Rh-NP) over graphite screen-printed electrodes (SPEs) for the determination of hydrogen peroxide in the presence of oxygen. Rh-NP, electrostatically stabilized by citrate anions, were immobilized over graphite SPEs, through coulombic attraction on a thin film of positively charged PEI. The functionalized sensors, polarized at 0.0 V vs. Ag/AgCl/3 M KCl, exhibited a linear response to H_2O_2 over the concentration range from 5 to $600 \mu\text{mol L}^{-1} \text{H}_2\text{O}_2$ in the presence of oxygen. The 3σ limit of detection was $2 \mu\text{mol L}^{-1} \text{H}_2\text{O}_2$, while the reproducibility of the method at the concentration level of $10 \mu\text{mol L}^{-1} \text{H}_2\text{O}_2$ ($n=10$) and between different sensors ($n=4$) was lower than 3 and 5%, respectively. Most importantly, the sensors showed an excellent working and storage stability at ambient conditions and they were successfully applied to the determination of H_2O_2 produced by autooxidation of polyphenols in tea extracts with ageing. Recovery rates ranged between 97 and 104% suggesting that the as-prepared electrodes can be used for the development of small-scale, low-cost chemical sensors for use in on-site applications.

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1. Introduction

The inherent advantages associated with the electrochemical detection of hydrogen peroxide (e.g. high sensitivity and selectivity, rapid response, low cost, simple instrumentation and easy miniaturization) have pushed methods based on electrochemical sensors and biosensors at the forefront of scientific research. Although a plentiful of electrochemical sensors based on Prussian blue [1,2] and other electrocatalysts [3–5], conducting polymers [6,7] and enzyme-based biosensors [3,8–10] have been developed, the drive over the last years is tipped in favor of metal nanoparticles (NP)-based sensors [11–13]. Such sensors offer unique advantages in terms of sensitivity, selectivity, compatibility with living organisms and working stability. Moreover, due to their ultra-fine dimensions and high electroactive surface area they provide unique opportunities for incorporation in miniaturized and low-cost substrates, thus giving rise to the provision of expedient solutions to the most contemporary demands in chemical sensing such as, on-site applications, in-vivo monitoring, tissue-embedded flexible sensor-based alarm systems etc [14,15].

A big obstacle to the use of metal NP-based hydrogen peroxide sensors is their inherent electrocatalytic activity to the reduction of dissolved oxygen, which restricts their use only in deaerated solutions. Beyond practical difficulties associated with sample deaeration outside the laboratory, deoxygenation of the sample may also affect the analysis due to volatility of H_2O_2 [16]. To date, the only NP-based electrochemical sensors that have been reported to enable the selective reduction of hydrogen peroxide in the presence of oxygen rely on phosphonate functionalized Pt nanoclusters [17] but they exhibit mediocre stability over time (~ 1 month) and their analytical utility has only been verified in standard solutions.

Among the vast gamut of nanoparticle-based electrochemical sensors, rhodium nanoparticles (Rh-NP) are the least represented. The only efforts made to exploit the potential utility of nanometer sized Rh particles in analytical applications focus on hybrid materials such as dendrimer-Rh-NP [18] and porous Rh nanotubes [19] for the detection of H_2O_2 , Rh-NP-loaded carbon nanofibers for the determination of hydrazine [20] and Rh-NP-carbon nanospheres for H_2 sensing [21]. Beyond the demanding synthetic efforts, all these sensors are still at an early stage of development and as such their use in real samples has not been evaluated. Additionally, oxygen removal from all solutions is necessary to alleviate its interference, which limits their application to on-site

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analysis. Therefore, there is a large gap regarding the realistic use of Rh-NP as electrochemical sensors.

In this work, we present for the first time an electrochemical sensor based on Rh-NP nanoparticles for the determination of H_2O_2 in complex samples in the presence of dissolved oxygen. The sensors were modified by a simple drop-casting deposition of Rh-NP on the surface of graphite screen printed electrodes. Immobilization was accomplished by electrostatic attraction between the negative surface charge of Rh-NP and positively charged polyethyleneimine (PEI) previously functionalized on the surface of the electrodes. A remarkable electrocatalytic response for the reduction of hydrogen peroxide was recorded, even in the presence of oxygen, thus alleviating the need for sample deaeration. The newly devised sensor was applied to monitor the H_2O_2 -generating ability of aqueous tea extracts, which is produced by autooxidation of polyphenols and may negatively affect living systems due to its pro-oxidant action [22]. The facile fabrication procedure along with the improved analytical performance in terms of selectivity, sensitivity and the exceptional working stability of the sensor under realistic conditions, suggest that Rh-NP hold great promise to the fabrication of low cost, disposable sensors for in-field detection of H_2O_2 .

2. Experimental

2.1. Materials

Citric acid, polyethyleneimine (PEI, branched, M.W. ~ 2000 by LS), and sodium borohydride were purchased from Sigma-Aldrich. Catalase from bovine liver (M.W. $\sim 240,000$, $\geq 200,000$ U mL^{-1}) and $\text{RhCl}_3 \times 3\text{H}_2\text{O}$ (38% in Rh) were obtained from Fluka and Merck, respectively. All other reagents were of analytical grade and were used without further purification. Double distilled water (DDW) was used throughout. A stock solution of approximately 0.1 mol L^{-1} H_2O_2 was prepared by appropriate dilution of the concentrated solution ($> 30\%$ H_2O_2 , Fluka) in DDW, stored at $+4^\circ\text{C}$ and was weekly standardized with the KMnO_4 titrimetric method.

2.2. Preparation of rhodium colloidal suspension

Rhodium nanoparticles were prepared according to an earlier work [23] by reducing $0.765 \text{ mmol L}^{-1}$ of $\text{RhCl}_3 \times 3\text{H}_2\text{O}$ with 5 mmol L^{-1} NaBH_4 in the presence of 0.5 mmol L^{-1} citrate ions, which were used as morphology regulators and stabilizers. After 15 min of mixing the color of the suspension turned to dark brown–green. Based on dynamic light scattering data, the average hydrodynamic diameter of the rhodium nanoparticles was found to be 8.7 nm (Fig. S1, Supporting information).

2.3. Fabrication of screen-printed electrodes

Low-cost, all-graphite screen-printed electrodes (SPEs) were fabricated over a $125 \mu\text{m}$ thick flexible polyester substrate (Mac Dermid) using a DEK 247 screen printer and polyester screens (280 mesh, DEK). Graphite ink (PF-407A, Acheson) was forced through a $13\text{--}20 \mu\text{m}$ thick emulsion with the desired pattern using a polyurethane 75 durometer squeegee. Before measurements, the conductive track was covered with an insulating tape (RS components). Details on the fabrication process are given in a previously published work [24].

2.4. Instrumentation

Cyclic voltammetry (CV), amperometry and electrochemical impedance spectroscopy (EIS) experiments were performed with the electrochemical analyzer Autolab PGSTAT12/FRA2 in a one-compartment three-electrode cell. Bare or modified SPEs and a platinum wire were served as the working and auxiliary electrodes, respectively. The reference electrode was a $\text{Ag}/\text{AgCl}/3 \text{ M KCl}$ (IJ Cambria) electrode and all potentials reported hereafter refer to the potential of this electrode. CV and amperometry experiments were performed in a solution of 0.1 mol L^{-1} phosphate buffer solution containing 0.1 mol L^{-1} KCl (PBS), pH 7, at room temperature, using a scan rate of 0.1 V s^{-1} and at a polarization potential 0.0 V (unless stated otherwise), respectively. The impedance spectra were recorded over the frequency range $10^{-1}\text{--}10^5 \text{ Hz}$, using a sinusoidal excitation signal, superimposed on a DC potential of 0.200 V . Excitation amplitude of 10 mV (rms) was used throughout. EIS measurements were performed in a solution 0.1 mol L^{-1} PBS, pH 7, at room temperature, in the presence of 5 mmol L^{-1} hexacyanoferrate (II)/(III) (1+1 mixture), which used as redox probe.

Scanning electron images and elemental microprobe analysis were performed on a JEOL JSM-6510LV scanning electron microscope equipped with an INCA PentaFETx3 (Oxford Instruments) energy dispersive X-ray (EDX) spectroscopy detector. Data acquisition was performed with an accelerating voltage of 20 kV and 60 s accumulation time. Samples were coated with a 15-nm -thick film of Au using a Polaron SC7620 sputtercoater by Thermo VG Scientific.

2.5. Preparation of the tea extracts

Tea samples (black and green) were purchased from the local market. An amount of 3.00 g of each sample was added in 50.00 mL 0.1 mol L^{-1} PBS pH 7, and the mixture was heated at 90°C for 30 min under stirring. The mixture left to cool at room temperature, centrifuged at 5000 rpm for 30 min and then filtered through a Millipore membrane ($0.45 \mu\text{m}$ pore size). For the recovery studies, the sample was fortified with 1.43 mmol L^{-1} H_2O_2 . Control samples were prepared in a similar manner by also adding $10 \mu\text{L}$ catalase.

2.6. Analytical procedure

A $(65.00 - x)\text{-mL}$ aliquot of PBS was introduced in the reaction cell and stirred at a moderate speed with a magnetic stirrer. When a stable current value was reached, appropriate amounts ($x\text{mL}$) of H_2O_2 or tea extract samples were added, and current changes due to the electro reduction of H_2O_2 at 0.0 V were recorded. The steady-state current response was taken as a measure of the analyte concentration.

Calibration curves at different working ranges were constructed by adding 5 (2 first additions), 10 (next 18 additions) and 100 (next 9 additions) $\mu\text{mol L}^{-1}$ H_2O_2 in the measuring cell.

3. Result and discussion

3.1. Electrochemical behaviour of SPEs/Rh-NP

The CV plots of bare and Rh-NP-modified SPEs in 0.5 mol L^{-1} H_2SO_4 deaerated solution are illustrated in Fig. 1. The pattern of the recorded CV can be explained as follows: In the hydrogen region, the sharp increase of the current at potential values more cathodic than -0.100 V can be collectively attributed to the adsorption of hydrogen ions and to the hydrogen evolution

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