INKJET-PRINTED ELECTRODE MODIFIED WITH MAGNETITE PARTICLES AND CARBON NANOTUBES FOR THE NON-ENZYMATIC AMPEROMETRIC DETERMINATION OF HYDROGEN PEROXIDE

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Introduction

Inkjet printing is a widely used printing technology for sensor manufacture because it allows low costs and high mass-production of reproducible devices [1-3], while it has the additional advantages of versatility and high resolution for the development of prototypes. However, when it comes to enzymatic biosensors, inkjet printing of enzymes presents some challenges, especially regarding molecular stability [4]. For that reason, there is a great interest in replacing enzymes by catalytic nanoparticles. In the particular case of the reduction of hydrogen peroxide, different nanomaterials have been proved to catalyze this reaction in a similar fashion as peroxidases, such as horseradish peroxidase. Either metal or metal oxides nanoparticles have been used in combination with carbon nanotubes (CNT) for the preparation of non-enzymatic electrodes. The incorporation of catalytic nanoparticles allows a sensitive quantification of H_2O_2, while CNT provide a conductive matrix and allow efficient electron transfer with the redox catalyst. Several electrochemical sensors of this sort have been reported, including Au/CNT, Ag/CNT, and Cu_2O/CNT composites, presenting moderate to high catalytic performance towards H_2O_2 without the need of both an enzyme and a redox mediator [5-7].

In this work, we present the results obtained for a non-enzymatic electrode printed with a single-walled carbon nanotubes (SWCNT) ink containing magnetite nanoparticles for the amperometric determination of hydrogen peroxide, which presented remarkable figures of merit.

Methods

Anhydrous ferric chloride ($FeCl_3$), trisodium citrate, anhydrous sodium acetate, ethylene glycol (EG), were of analytical grade and used as received. Fe_3O_4

particles were synthesized via a modified solvothermal method as previously reported by Deng et al. [8]. Firstly, 1 mmol of $FeCl_3$ and 0.4 mmol of trisodium citrate were placed in 20 ml of EG in a closed flask under magnetic stirring. After complete dissolution of the reactants, 20 mmol of sodium acetate and 200 µL of miliQ water were added, turning the solution from an intense yellow to pale red brown after 1 hour. Then, the solution was loaded into a 25 ml Teflon-lined stainless-steel autoclave reactor, sealed, and placed in an oven at 200 °C for 12 hours. After letting the reactor cool to room temperature, the black product was washed several times with miliQ water with the assistance of a neodymium magnet. Finally, the particles were resuspended in 5 ml of miliQ water. Scanning electron microscopy (SEM) images were taken with a FEI Quanta 250 after solvent evaporation of drop casted dispersions. X-ray diffraction (XRD) patterns were obtained with a standard Rigaku diffractometer with CuKα radiation.

A waterborne ink was prepared containing 0.9 mg/ml SWCNT and 0.9 mg/ml Fe_3O_4 particles. A three-electrode electrochemical cell was fabricated on a 125 µm thick polyethylene terephthalate substrate, without any extra surface treatment, using a DoD Dimatix Materials Printer. For the development of the conductive path of the working electrodes (WE) with a geometric surface area (GSA) of 0.78 mm^2 and counter electrode (CE) with a GSA 5.25 mm^2, a commercially low curing Au nanoparticle ink was used. For the reference electrode (RE), a Ag|AgCl printed electrode was used. The passivation and protective layer of the electrodes was done using a dielectric PriElex® SU-8 ink. Finally, a circular area with diameter of 1 mm was printed onto the WE with the carbon nanotubes water-based ink. Electrochemical measurements were carried out using an 8-channel potentiostat 1030A Electrochemical Analyzer (CH Instruments, USA) in 0.1M phosphate buffer of pH 7.4 at an applied potential of -0.2 V at room temperature in quiescent solutions.

Results

Fig. 1a shows SEM images of magnetite nanoparticles synthetized by the solvothermal method. These citrate-stabilized nanoparticles, 80 nm in average diameter, are in fact formed by clusters of smaller nanoparticles, as demonstrated by the crystal size obtained from de XRD pattern (Fig. 1b). The NPs were mixed with a SDS-stabilized SWCNT dispersion to obtain a waterborne ink which was used to print a sensitive layer toward hydrogen peroxide onto printed gold electrodes (Fig. 2).
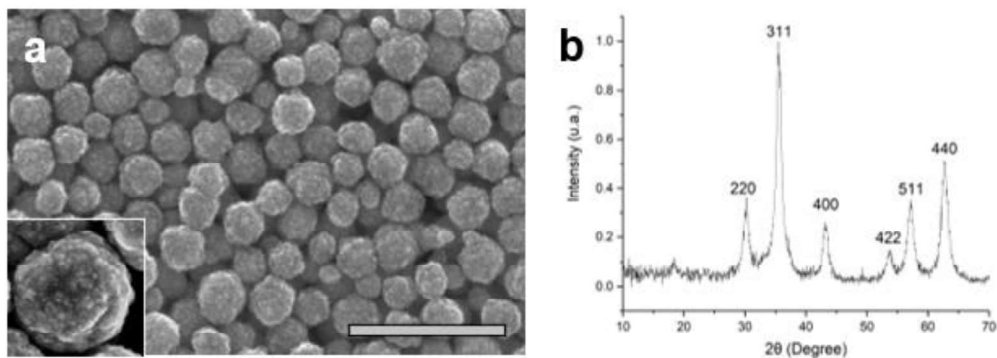
Fig. 1. SEM images (a) and X-ray diffraction pattern (b) of Fe_3O_4 particles. Bar scale = 400 µm.
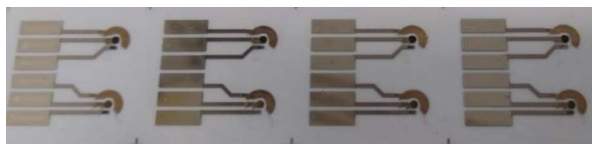

Fig. 2. Optical image of inkjet-printed non-enzymatic electrodes.

Fig. 3a shows the calibration curve obtained at low hydrogen peroxide concentration. A linear relationship was found with a sensitivity of 680 µA M^{-1}. The limit of detection and the limit of quantification, calculated from the standard deviation of a blank solution, were 30 µM and 100 µM, respectively. It is worth noting that the non-enzymatic electrode presented a quasi-linear response (current approx. proportional to concentration) over several orders of magnitude, up to almost 1 M.
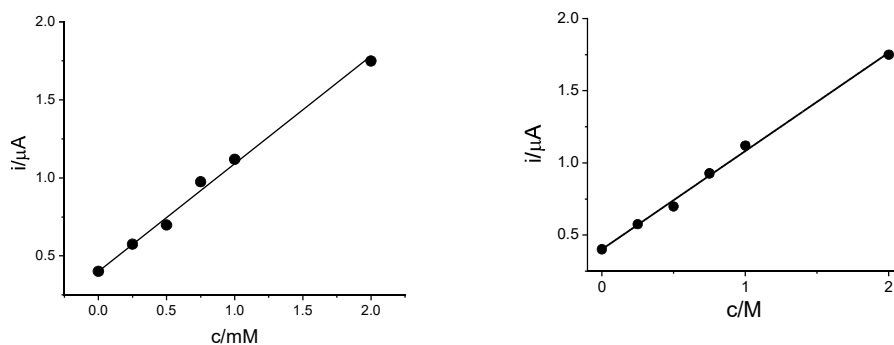

Fig. 3. Dependence of measured current with hydrogen peroxide concentration for millimolar and sub-millimolar concentration range (a) and from sub-millimolar to molar range (b, log-log plot).

A log-log plot (Fig. 3b) revealed that the experimental points could be fitted to a power function of the type $i = m\,c^n$, where i is the current, c is the concentration, m is a parameter related to the sensor's sensitivity, and n is an exponent or power parameter. A value of $m = 0.86$ was found for the exponent, whereas $m = 1$ would be expected for a true linear response.

Conclusions

In this work, we presented the preparation of an inkjet-printed non-enzymatic electrode for the amperometric determination of hydrogen peroxide, employing an ink containing SWCNT and magnetite particles. The sensor presented remarkable figures of merit, with a quasi-linear range of more than three orders of magnitude, from sub-millimolar concentration to almost 1 M, and a limit of detection of 30 µM.

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