Nanowire Ordered Arrays for Electrochemical Sensing of H2O2

Bernardo Patella, Rosalinda Inguanta, Salvatore Piazza, Carmelo Sunseri

Laboratorio di Chimica Fisica Applicata, Dipartimento di Ingegneria Chimica Gestionale Informatica Meccanica,
Università di Palermo, Viale delle Scienze, 90128 Palermo (Italy)
bernardopatella@yahoo.it

In this work, we present the performance of nanostructured array of Cu for electrochemical sensors of hydrogen peroxide. Nanostructured sensors are obtained by template synthesis in commercial polycarbonate membranes. Arrays of Cu nanowires were fabricated through a displacement deposition reaction that permits to obtain nanostructures directly and without the use of an external power supply. To test the performance of nanostructured sensors, electrochemical experiments were carried out in an aqueous solution with different amounts of hydrogen peroxide. In order to obtain sensors with stable performance, we found that it is essential to increase wettability of the nanostructures through addition of pure ethanol to the test solution. The main advantages of these electrodes are related to the high specific area (about 70 times higher than the geometrical one), which allows a low detection limit (less than 20 μM).

1. Introduction

Detection of hydrogen peroxide is very important in several fields because, owing to its oxidizing and reducing properties, this compound is widely used for treatment of waste water, paper and contaminated soil (Belinka, 2015) and also in medical applications (Ningthoujam, 2011). The most used methods for detection of hydrogen peroxide are IR spectroscopy, spectrophotometry and redox titration. These methods are often uneconomical or have very high detection time (Giomo et all, 2010). Instead, electrochemical sensors are cheap and detection time is lower than 3s; they are also reliable and easy to produce. Among electrochemical sensors, the most used are the amperometric ones that allow to obtain easily the calibration curve. A great advantage of amperometric sensors is that applied potential is close to 0 V, so that they can work with very low cost of management.

Electrochemical sensors detect the presence of hydrogen peroxide due to a redox reaction occurring at the electrode/electrolyte interface. Consequently, performance of the sensor will be improved by a greater electrochemical active area. For this reason, use of nanostructures, such as nanowires, nanotubes or nanoparticles, allows to improve considerably the performance of the sensor because of their very high surface area. Aim of this work was to investigate template synthesis, and in particular the galvanic deposition method, as an easy and direct technique for fabrication of nanostructured electrodes with very large active area. The nanostructured electrodes were obtained by a two-step procedure that allows to obtain an array of nanostructures (fabricated by galvanic deposition) on a thin current collector, made of the same material, electrodeposited previously. Following this procedure, we have obtained nanoelectrodes of Cu and Pd very stable mechanically; subsequently they were assembled and tested as electrochemical sensors.
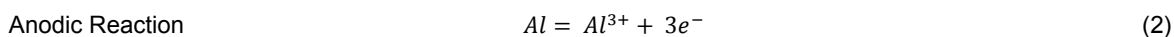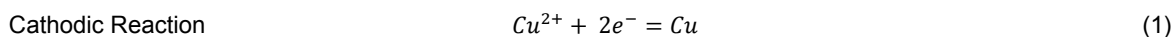
In this work attention is focused to overcome some drawbacks characterizing nanostructured electrodes. The principal drawback is the low wettability of the nanostructures that are subject to the well known lotus effect. In fact due to their very high roughness, aqueous solvent is not able to soak the entire surface area of the array limiting performance (Yuxiang et all, 2015). This problem can be limited using a secondary solvent (like ethanol) or surfactants, in order to decrease surface tension of the solution. Another problem of electrochemical sensors is their short lifetime: in fact modification of sensor surface, attributable to oxidation or hydration phenomena, causes a decrease of the sensing properties (Kurowska et al., 2009). This problem is enhanced in the case of nanostructured electrodes owing to their high activity and surface area. In order to

increase lifetime of the sensor it is essential to select suitable storage conditions (temperature and storage solution composition). For this purpose also a periodic cleaning treatment is helpfull. Here, we present the experimental procedures adopted to overcome the above problems and the preliminary results regarding the sensing properties of Cu nanoelectrodes. In particular, chronoamperometric and calibration curves and selectivity tests are reported and discussed.

2. Experimental

Fabrication of Cu nanostructures was performed following a two-step procedure described in detail elsewhere (Inguanta et al., 2009a, 2011, 2012; Battaglia et al., 2013). Briefly, polycarbonate membranes (Poretics, GE Osmonics) were used as template for the deposition of nanostructures. Because membrane is not conductive, prior to fabrication of the electrodes, one surface was sputtered with a very thin layer of gold. Subsequently, a layer of copper (about 12 μm thick) was eletrodeposited. This layer plays two key roles: it serves as a current collector, ensuring ohmic contact for the subsequent galvanic deposition, and also as mechanical support for the nanostructures. This copper layer was obtained in a two electrodes cell (counter electrode a Pt mesh) at 8 mA/cm^2 and room temperature using a 0.2M CuSO$_4$·5H$_2$O and 0.2M H$_3$BO$_4$ aqueous solution having pH=3.9. Depositions were performed using a PAR potentiostat/galvanostat (PARSTAT, mod. 2273).

For the galvanic deposition of nanostructures, current collector was coupled electrically through a conductive paste with an aluminium tube, previously polished with emery paper. The bi-metallic couple was immersed in an electrolytic solution containing copper ions. In this way, the following reactions take place:

Cathodic Reaction $\qquad\qquad\qquad\qquad\qquad Cu^{2+} + 2e^- = Cu$ (1)

Anodic Reaction $\qquad\qquad\qquad\qquad\qquad Al = Al^{3+} + 3e^-$ (2)

Thus dissolution of aluminum, which acts as sacrificial anode, produces electrons for copper deposition inside the channels of the polycarbonate membranes. Deposition solution was a 0.1M CuSO$_4$·5H$_2$O and 0.05M H$_3$BO$_4$ aqueous electrolyte at pH=2. Galvanic deposition was carried out for different times, from 20 to 40 minutes, in order to vary nanostructures length. Besides, in order to control deposition rate also the effect of the ratio between anodic and cathodic area was evaluated. At the end of the galvanic growth, samples were etched in pure di-chloromethane for removing the template.

Morphology was analyzed through scanning electron microscopy (SEM), using a FEI FEG-ESEM (mod. QUANTA 200) equipped with an Energy Disperse Spectroscopy (EDS) detector. Cyclic voltammetry (CV) measurements were performed to found the suitable applied potential for the subsequent cronoamperometric tests (Min Han et al., 2012). For CV test, the range of potential from -0.6 V to +0.3 V was analyzed with a scan rate of 50 mV/s. CV experiments were performed both in absence of hydrogen peroxide and with 0.1mM of H$_2$O$_2$. A three-electrode cell was employed, having a Pt mesh as counter electrode and a Ag/AgCl as reference electrode. All potentials given below are referred to Ag/AgCl. Sensor calibration curve was obtained through amperometric tests carried out in a stirred solution, analyzing a range of H$_2$O$_2$ concentration from 0M to 1M. The electrochemical tests were performed in 0.2M phosphate buffer solution (PBS). Current vs. time curves were recorded continuously during sequential additions of different concentration of H$_2$O$_2$. In order to increase nanstructures wettability, some tests were performed using equivolumetric solutions of 0.2M PSB and pure ethanol.

From the linear range of the calibration curve, sensitivity and limit of detection (LOD) of the sensor were obtained. To calculate LOD, the following equation was used (Di Natale, 2004)

$$LOD = 3\frac{\sigma}{S}$$ (3)

where σ is the standard error (μA) of the calibration line and S is the sensitivity (μA/μM). The selectivity of nanostructured sensors towards glucose, ascorbic acid, uretic acid and potassium oxalate was verified. Besides, accuracy and reproducibility of sensors were tested. The accuracy was calculated according to the equation (Kalantar et al., 2008):

$$\varepsilon = \frac{Cm - Cv}{Cv} * 100$$ (4)

where ε is the accuracy percent, C$_m$ is the predicted concentration and C$_v$ the real concentration. Some electrochemical tests were carried out also using a thin film of copper for comparing performance of the nanostructured electrodes. After each experiment, electrodes were stored in PBS solution.

3. Results and discussion

Galvanic deposition is a fast and simple process ($\approx$ 60 minutes for each electrode) that permits to obtain electrodes consisting of Cu nanowires arrays having different length (from 1.6 μm to 3 μm, depending on deposition time). Morphology of the nanostructures obtained by galvanic deposition is influenced by several parameters, like bath composition, pH, anodic to cathodic area ratio, deposition time (Inguanta et al., 2009b). During galvanic deposition it is important to control hydrogen evolution, because this reaction has a key influence on mechanical stability and shape of nanostructures, permitting formation of both nanowires and nanotubes. Thus, it is essential to select a suitable pH that in our case was around 2. Baths with pH > 2 were excluded because they hinder Al dissolution, whilst at very acidic pH hydrogen evolution reaction becomes predominant with respect to deposition of metal. Also bath composition plays an important role. In particular, we found that the best choice is a solution containing 0.1M of copper salt and 0.05M of boric acid. Galvanic depositions carried out in more concentrated baths lead to nanowires with non uniform length. This is due to the higher driving force that causes different growth rate in different template channels. Another parameter investigated is the ratio between cathodic and anodic area. The best value was found equal to 0.065: a lower ratio implies fast kinetics of deposition and thus nanowires with non uniform length. On the contrary, for values above 0.065 deposition is very slow. Thus, we employed anodic (aluminum) and cathodic (membrane) areas of 22 cm^2 and 1.44 cm^2, respectively. Under these experimental conditions, copper deposition occurs in a time shorter than that reported in a previous work (Inguanta et al., 2008). In particular, nanostructures reach the top of the membrane (length: 6 μm) after about 70 minutes. It is important to highlight that length of nanowires can be controlled by deposition time. SEM images of Figure 1 show morphology of Cu nanostructures.
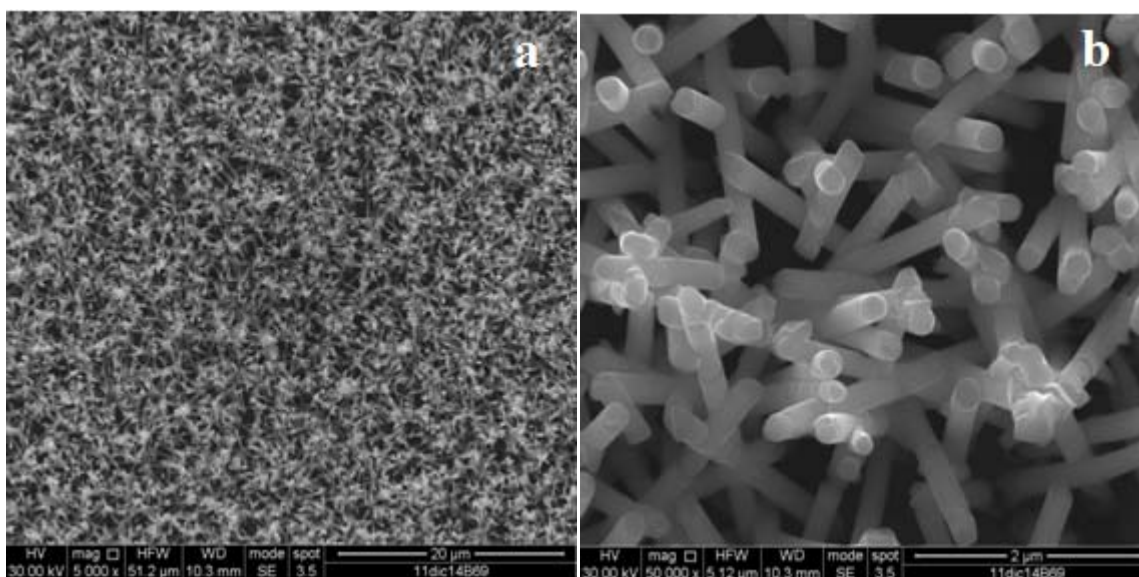

Figure 1: Cu nanowire array obtained after 40 minutes of deposition.

From Figure 1 it appears that NWs are straight with a cylindrical shape and uniformly distributed over the current collector surface. Their diameter (about 220 nm) is almost equal to the mean diameter of template pore, and the mean length is about 3 μm after 40 min deposition. Chemical composition of the nanowires was evaluated by EDS spectroscopy showing the presence of Cu and Au peaks only.

These nanostructured electrodes were sealed with an insulating lacquer to obtain a geometric area of about 3.9 cm^2 and tested as electrochemical sensors for hydrogen peroxide. We have found that it is essential performing the electrochemical tests in a solution containing PBS and ethanol in order to measure a stable sensing response. In fact, as reported above, use of ethanol is necessary to improve wettability of the nanostrucuteres. Based on cyclic-voltammetry experiments, carried out both in presence (0.1mM) and in absence of hydrogen peroxide, we have selected a potential equal to -0.2V vs. Ag/AgCl for performing chronoamperometry, selectivity, accuracy and reproducibility tests.

Figure 2 shows the cronoamperometric response of an array of Cu nanowires obtained after 40 min of galvanic deposition. This curve was obtained by successive additions of small volumes of H$_2$O$_2$ solution at different concentrations to a 0.1M PBS solution continuously stirred. It can be seen that sensor responds

instantaneously after injection of H_2O_2. In fact, a sudden increase of cathodic current is observed followed by a fast stabilization to a new value.
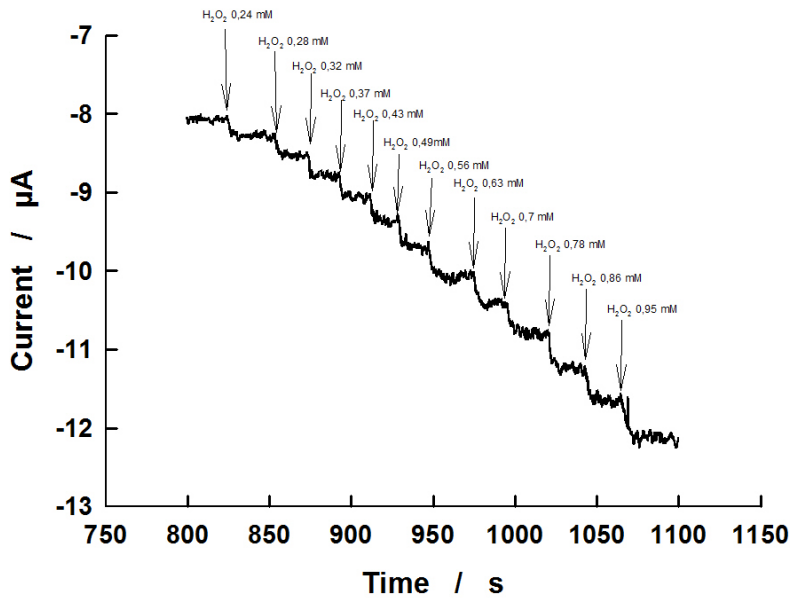

Figure 2: Amperometric response of the Cu NWs electrode of Figure 1 in the range from 0.24mM to 0.95 mM of H_2O_2
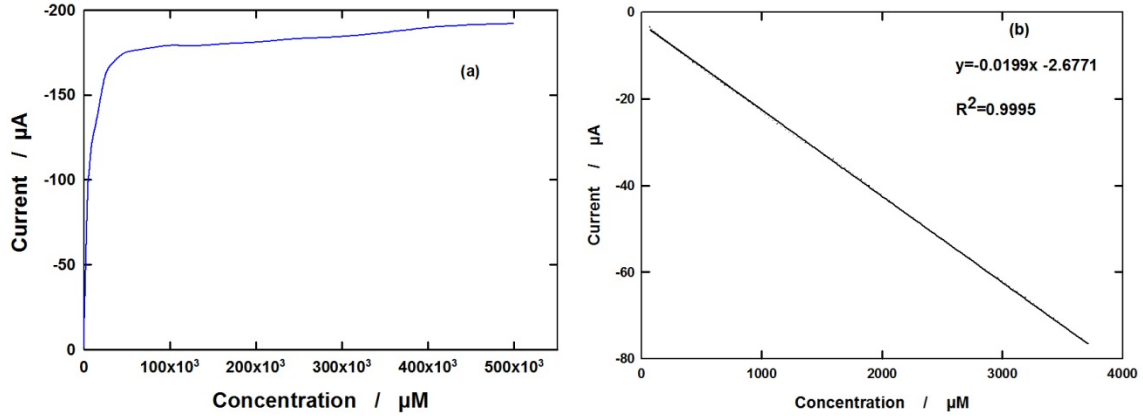

Figure 3: a) calibration curve and b) calibration line of Cu-NWs electrode of Figure 1

Table I. Performances of Cu NWs and Cu-film sensors.

	Linearity Range (µM)	LOD (µM)	Selectivity (µA/ µM cm^2)
Thin film	145-780	19.4	-0.1678
NWs- main length 3 µm	60-3700	13.8	-0.509

Figure 3 displays the calibration curve of the nanostructured electrode: a linear response from 60µM to 3700 µM was obtained. All calibration curves were obtained with a R^2 coefficient greater than 0.999 and with a very good sensitivity (about -0.509 µA/ µM cm^2). For comparison, in Table I range of linearity, selectivity, and LOD are reported for both Cu nanowires and film sensors. Results of Table I show clearly a noticeable increase of sensing performance when passing Cu thin film to a nanostructured system. This increase is due to the big enlargement of the electroactive area.

Selectivity tests towards the contaminants usually present with hydrogen peroxide (Kurowsla et al., 2013) were also performed. In particular, ascorbic acid, uretic acid, potassium oxalate and glucose were added at two different concentrations (1mM and 2mM). These contaminants were introduced after stabilization of the current due to addition of 1 mM (first step) and 2 mM (second step) of H_2O_2. As can be seen in Figure 4, a sharp current response is observed after the addition of H_2O_2, whilst response current remains almost constant after the addition of ascorbic acid, uretic acid and glucose. A very low increase of current was observed in the case of potassium oxalate. It is important to highlight that the presence of these interfering substances does not influence the correct operation of the sensor. In fact, further injection of H_2O_2 to the solution with the contaminants produces the expected stepwise increase of cathodic current.
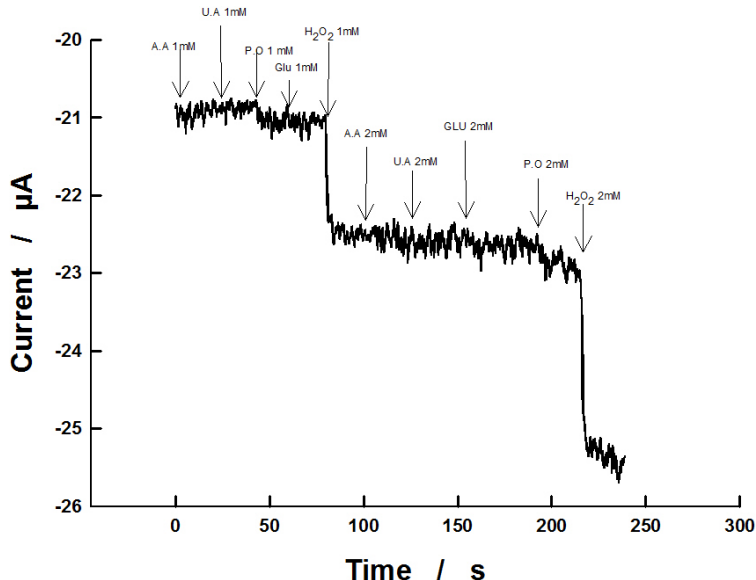

Fig 4: Selectivity test of Cu-NWs electrode of Figure 1

Thus from Figure 4 it is possible to conclude that Cu-NWs sensor is extremely selective toward hydrogen peroxide.

4. Conclusions

We have found that it is possible to obtain nanostructured electrodes of Cu by means of a simple galvanic deposition inside pores of a polycarbonate membrane template. Nanostructured electrodes were obtained by a two-step procedure that permits to obtain nanowires well attached to a compact film of Cu, acting both as current collector and as mechanical support of the nanostructures.

These electrodes were tested as electrochemical sensors using a solution of 0.2M PBS and ethanol to improve wettability of the nanostructures. In comparison to a massive Cu electrochemical sensor, which has lower limit of linearity greater than 100μM and upper limit lower than 800 μM, our sensors are able to detect the presence of hydrogen peroxide at concentrations lower than 70 μM and higher than 3500 μM. This improved performance is attributable to the large surface area of nanostructures (about 70 times higher than the geometrical one).

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