Preliminary studies on the iodide determination in the marine environment by nanoelectrode ensembles

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ABSTRACT Ensembles of gold nanodisk electrodes (NEE - Nano Electrodes Ensemble) 30 nm in diameter are presented, focusing on their capability of furnishing improved signal/background current ratios with respect to conventional electrodes. NEEs are employed here for the voltammetric determination of iodide concentration in samples of interest in marine environmental studies. Specifically, NEEs are applied to determine directly the iodide at micromolar concentration levels in iodized edible salt by cyclic voltammetry as well as at sub-micromolar concentration levels in lagoon waters by square wave voltammetry.

1. Introduction

The synthesis of new nanostructured materials and the study of their properties (electrochemical, catalytic and optical) compared to those of macroscopic samples of the same materials, are attracting increasing interest in modern chemical science. The transition between bulk and molecular scales often leads to dramatic changes in the properties of a material, which can be interesting for practical applications in a variety of areas, including chemistry, physics, electronics, optics, materials and biomedical sciences. This trend includes the preparation, characterization and electrochemical applications of electrodes with critical dimensions in the nanometer range (Hulteen and Martin, 1997; Foss, 2002; Ugo *et al.*, 2002). Among other more complex and expensive procedures, the preparation of nanoelectrodes using nanoporous membranes as templates distinguishes itself for its simplicity and wide applicability (Menon and Martin, 1995).

The use of pre-formed microporous membranes as templates for the synthesis of nanomaterials was somehow a revolutionary step since it made a simple but effective procedure for the easy preparation of nanomaterials accessible to almost any laboratory. What is needed for the membrane-based synthesis of nanomaterials is, in fact, a very simple apparatus, such as an apparatus for metal deposition and basic electrochemical instrumentation.

The nanoelectrode ensembles (NEEs) used in our laboratory are prepared by the electroless deposition of gold electrode elements within the pores of a microporous polycarbonate membrane (De Leo *et al.*, 2007). The diameter and length of the pores in the template determines the geometrical characteristics of the metal nanostructure with radii as small as 30 nm. A sketch showing the structure and geometric characteristics of these NEEs is reported in Fig. 1.

For NEEs operating in total overlap diffusion conditions, the signal is proportional to the overall geometric area of the ensemble (A_{geom}), while the background capacitive current (that is the main component of the noise) is proportional only to the active area (A_{act}). Because of NEEs'

geometrical characteristics, the ratio A_{geom}/A_{act} is as high as 10^2-10^3, so that signal/background current ratios are enhanced and detection limits improved by 2-3 order of magnitude. Experimental results show that this is true for a series of analytes dissolved in water (Ugo *et al.*, 2003; Moretto *et al.*, 2004; Ugo, 2006). In the present study, we will extend the possibility of using NEEs for trace analyses of iodide (Pereira *et al.*, 2006) in samples of interest in marine studies.

Iodine is a trace element present in seawater and sea products mainly in the form of iodide or iodate anions (Wong and Zhang, 2003). For human beings, iodine is an essential component. It is required by the thyroid gland to produce two iodized hormones, thyroxine and tri-iodothyronine, which are used by the body during metabolism. The human body does not need much iodine and, on average, contains around 20-25 mg of the element. When starved for iodine, the thyroid gland swells and this causes goiter.

The most common sources of iodine intake are table salt and seafood, but also other food can contain iodine such as plants grown in iodine-rich soils. However, in certain parts of the world the soil contains no iodine, hence the plants lack iodine and iodine deficiencies in the diet can cause health problems (Pongpaew *et al.*, 2002; Delange, 2005).

By taking advantage of the electroactivity of iodide, cathodic stripping methods have been applied (Luther III *et al.*, 1988; Zimmermann, 2008). However, for quick analytical control of the environment, direct methods (which could avoid a pre-concentration step) are preferable.

Recent research (Ugo *et al.*, 2003; Moretto *et al.*, 2004; Ugo, 2006; De Leo *et al.*, 2007) has shown that the use of NEEs can improve the performance of electrochemical determinations; therefore, in the present work, we examine and discuss the possible use of NEEs for the direct electroanalysis of iodide, in real samples such as iodised table salt and lagoon waters.

2. Experimental

2.1. Materials

Polycarbonate filtration membranes (SPI-Pore, 47 mm filter diameter, 6 μm filter thickness) with a nominal pore diameter of 30 nm and coated with the wetting agent polyvinylpyrrolidone were used as templates to prepare the NEEs. Commercial gold electroless plating solution (Oromerse Part B, Technic Inc.) containing 0.32 M $Na_3Au(SO_3)_2$, 5 M Na_2SO_3, was diluted (40 times with water) prior to use.

All other reagents were of analytical grade and were used as received. Purified water was obtained using a Milli-Ro plus Milli-Q(Millipore) water purification system.

2.2. Instrumentation

Cyclic voltammetric (CV) measurements were carried out at room temperature (22±1°C) using a three-electrode single-compartment cell equipped with a platinum coil counter electrode and an Ag/AgCl (KCl saturated) reference electrode. All potential values refer to this reference electrode. A CH660A (CH Instruments Inc, USA, commercialized in Europe by IJ Cambria, UK) apparatus controlled via PC by its own software was used for voltammetric measurements.

2.3. Preparation of the electrodes

The nanoelectrode ensembles were prepared using the electroless plating procedure described

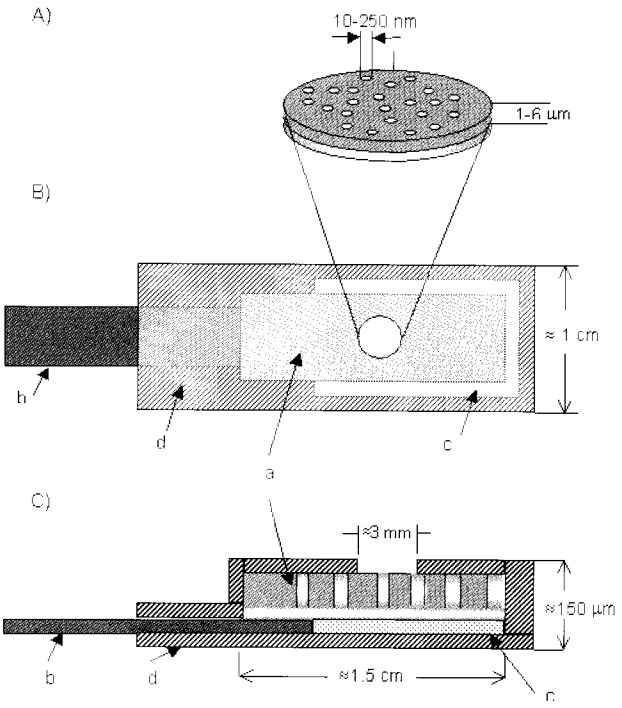

Fig. 1 - Scheme of an Au-NEE prepared using a track-etched polycarbonate membrane as template. A) particular of the section of the active area; B) top view, C) section of all the NEE ready for use as a working electrode. (a): track-etched golden membrane; (b): copper adhesive tape with conductive glue to connect to instrumentation; (c): aluminium adhesive foil with non-conductive glue; (d): insulating tape. Note: the dimensions of the pores (nanofibers) are only indicative and not in scale.

previously (De Leo *et al.*, 2007). Briefly, after wetting in methanol for 2 hours, the polycarbonate template membrane was sensitized with Sn^{2+} by immersion in a solution that was 0.026 M in $SnCl_2$ and 0.07 M in trifluoroacetic acid in 50:50 methanol-water for 5 minutes. After rinsing with methanol for 5 min, the sensitized membrane was immersed for 10 min in 0.029 M $Ag[(NH_3)_2]NO_3$. The membrane was then immersed in the Au plating bath which was 7.9×10^{-3} M in $Na_3Au(SO_3)_2$, 0.127 M in Na_2SO_3. After waiting 30 minutes, 0.625 M formaldehyde was added to the plating bath; this delay time was introduced here since it allows one to separate the formation of the first gold nuclei (produced by galvanic displacement of metallic Ag° nuclei with Au° nuclei) from the following catalytic growth of these nuclei by further gold deposition caused by the formaldehyde. The temperature of the bath was 0-2 °C. The electroless deposition was allowed to proceed for 15 hours, after which an additional 0.3 M formaldehyde was added. Deposition was continued for another 9 hours, after which the membrane was rinsed with water and immersed in 10% HNO_3 for 12 hours. The membrane was then rinsed again with water and dried. The final assembly of the NEEs, was obtained using previously published procedures (Menon and Martin, 1995) and a later modification (Ugo *et al.*, 2003); a scheme sketching the structure of the NEEs obtained is shown in Fig. 1.

The geometric area, A_{geom}, of the NEE (0.07 cm^2) is determined by the diameter (3 mm) of a hole punched in a layer of insulating plastics (Monokote by Topflite) that covers the upper face (peeled) of the NEE [part (d) in Fig. 1].

Conventional "macro" gold electrodes, hereafter named "Au-macro" for brevity, were

prepared from a golden glass plate (thickness 1 mm) coated with nickel 80 Å, chromium 20 Å and gold 3900 Å on the outer surface. They were purchased from ACM France. The golden plate was cut into slides (ca. 2.5 cm x 1.0 cm) and the geometric area of the electrodes (0.07 cm^2) was defined, as it was made for the NEE, by the diameter of a hole punched in a strip of insulating tape which covers all the golden surface apart from the hole. The electrical contact was made with a copper tape before placing the insulating tape.

Before each set of measurements, the surface of the Au-macro electrodes was cleaned electrochemically by cycling in 0.5 M H_2SO_4 between -0.1 V and 1.5 V at 100 mV/s.

2.4. Samples

2.4.1. Edible salt

The edible table salt analyzed here was commercialized as iodized table salt and was sold by a local grocery shop. The declared iodide content was 3 mg of potassium iodide in 100 g of salt. The sample was prepared by dissolving 38.5 g (approximately equivalent to one mole of NaCl) of the salt in 250 mL of sulphuric acid, pH 1.0, and an aliquot (400 mL) of this solution was added to 20 mL of 0.1 M sulphuric acid, pH 1.0, in the electrochemical cell.

2.4.2. Lagoon water

Lagoon waters sampled at about a 25 cm depth in preconditioned bottles, in the Giudecca Channel, Venice. Samples were filtered through a 0.45 mm Millipore membrane and acidified with some drops of concentrated sulphuric acid to approximately pH 1.

3. Results and discussion

3.1. Table salt

Fig. 2A shows the CVs recorded at an NEE in 0.1 M H_2SO_4 supporting electrolyte before (dashed line) and after (dash and dotted line) the addition of 400 µl of table salt solution; the full line CV in the same figure was recorded after a further addition of 3.6 µM of iodide. An anodic current is indeed observed in the 550-700 mV region after adding the sample. A peak, although rather broad, is better detected in the same potential region after spiking with an 3.6 µM iodide (full line). Comparison with the literature (Pereira *et al.*, 2006) indicates that this peak is related to the electrochemical oxidation of I^- to I_2 at the Au-nanodisk electrodes.

The $E_{1/2}$ value, calculated as $(Ep_f+Ep_b)/2$ (where the *f* and *b* subscripts indicate the forward and backward peaks, respectively) was 540 mV and the forward-to-backward peak separation (ΔE_p) values were of the order of 250 mV. These values indicate a less reversible process in this kind of sample than in the synthetic ones, previously studied (Pereira *et al.*, 2006), since the forward to backward peak separation increased from 150 mV (synthetic sample) to 250 mV (spiked table salt). Anyway, the oxidation peak current increases by performing standard additions of known concentrations of iodide, so that the oxidation peak current values can be used for analytical purposes. The lower electrochemical reversibility of the CVs in the table salt sample is probably due to the presence of other components, such as anticaking agents, which are typical of this rather complex sample.

The iodide oxidation peak current was measured in the sample solution before and after

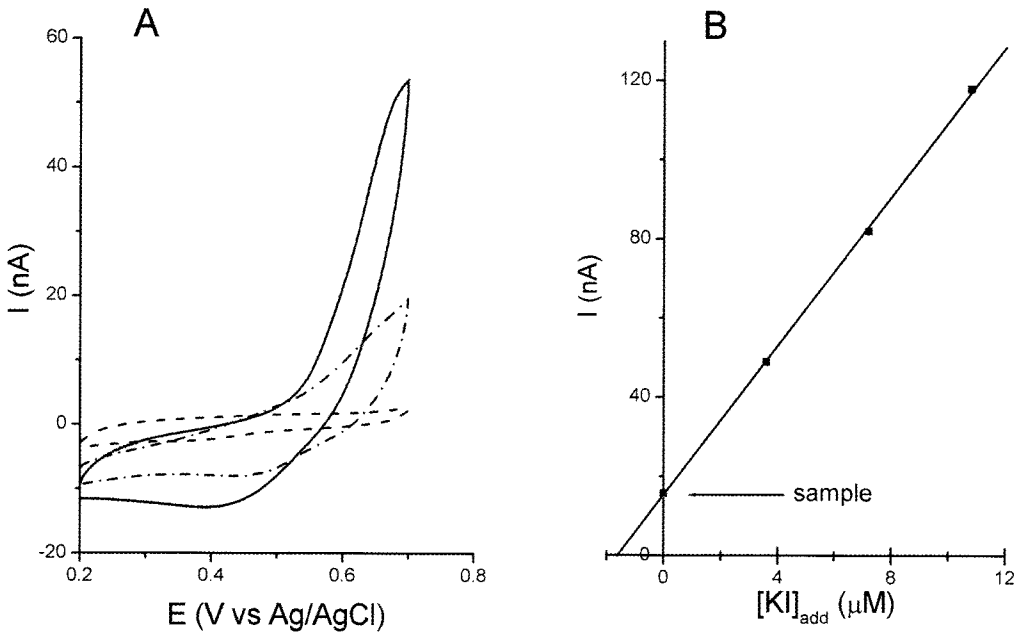

Fig. 2 - (A) Cyclic voltammograms recorded at 20 mVs^{-1} at a NEE in 0.1 M H_2SO_4 (---); acidified table salt solution, pH 1.0 (-·-·-) and spiked with 3.6 μM KI solution (-). (B) Standard additions plot.

spiking with known amounts of iodide. The standard addition plot is shown in Fig. 2B, where the intercept on the Y-axis corresponds to the oxidation peak current in the unspiked sample. From the intercept on the X-axis of the linear plot ($R^2 = 0.9996$) obtained, by simply changing the sign of the intercept, one can calculate the analyte concentration in the raw sample. In our case, the iodide concentration in the iodized table salt was 1.6 ± 0.3 μM (range on three replicate analyses). This value is slightly smaller (-24%), but in acceptable agreement with the 2.1 μM values calculated from the iodide contents and declared by the producer. The declared value corresponds indeed, to the amount of iodide initially added during the manufacturing of the table salt. Note that the recovery of the NEE-based method was previously evaluated as being approximately 98% (Pereira *et al.*, 2006), so that the smaller value determined here is indicative of a real lowering of the iodide content with respect to the declared value. This is not surprising since, in these kinds of samples, the iodide content can decrease during storage as a consequence of partial volatilization following spontaneous oxidation of iodide to iodine (Svancara *et al.*, 2002; Muranov *et al.*, 2004).

3.2. Lagoon water

The CVs recorded with NEEs in a acidified water sample from the lagoon of Venice showed a small signal at the potential values expected for the electrochemical oxidation of iodide to iodine in the anodic region. This signal increased by spiking the sample with standard additions of iodide. The lagoon water samples were acidified to pH 1 by adding a few drops of concentrated H_2SO_4. The iodide voltammetric behaviour, particularly the one observed after spiking the

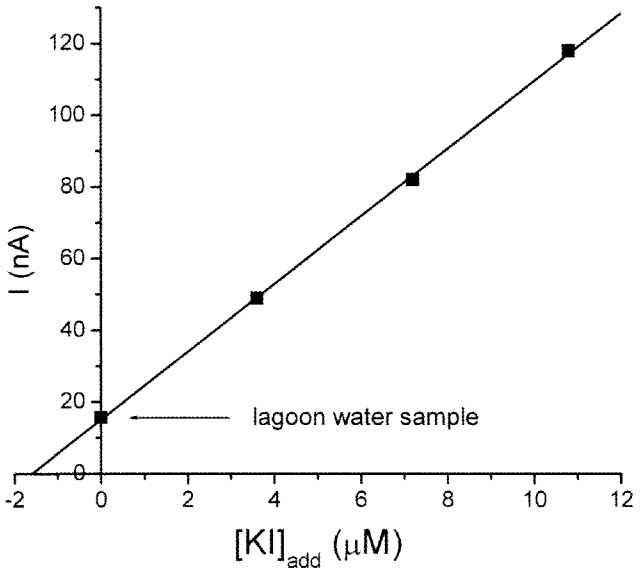

Fig. 3 - Standard additions plot from cyclic voltammograms recorded at an NEE at 20 mV/s in acidified lagoon water, before and after spiking with KI.

sample, is very similar to the one observed in the edible salt samples, however, here the signal in the unspiked sample is smaller. The standard addition plot reported in Fig. 3, allowed us to estimate a I^- concentration in the sample of 1.6 ± 0.5 μM (203 ± 63 μg/l) for triplicate analysis. This value is affected by a quite high imprecision (± 30 %) and the average value is slightly higher than the concentration values determined in the waters of the Venice lagoon by Marengo *et al.* (1995), who reported values between 14 and 32 μg/l. This raher high imprecision can be explained by taking into account that the typical iodide concentration in seawaters, including lagoon and estuarine waters (Wong and Zhang, 2003) is perhaps too close to the detection limit achievable by cyclic voltammetry with NEEs, that is 0.3 μM, i.e. 38 μg/l (Pereira *et al.*, 2006).

This prompted us to improve DLs for iodide determination with NEEs by using pulsed voltammetric techniques instead of a simple CV. It was recently demonstrated that differential pulse voltammetry improves detection limits at NEEs by more than one order of magnitude (Moretto *et al.*, 2004). Preliminary tests indicated that a similar effet can be obtained by using square wave voltammetry (SWV) with NEEs. On this basis, we applied SWV in the lagoon water samples. Fig. 4 shows the SWV recorded at an NEE in acidified lagoon water before (curve a) and after spiking with known amounts of iodide (curves b and c). Using the frequency and pulse height previously optimized by preliminary tests, a resolved peak is indeed detected at 600 mV vs Ag/AgCl, whose height scales with the KI standard additions. From the intercept point on the concentration axis of the standard addition plot (see Fig. 4 B, correlation coefficient 0.993) the iodide concentration in the sample turned out to be 0.60±0.06 μM (76±7 μg/l). These value are in the same order of magnitude as previous results in the same area (Marengo *et al.*, 1995). From the standard deviation of the intercept (σ) of the calibration plot and the slope of the same plot (m), the detection limit *DL* was calculated as $DL = 3\sigma/m$ and resulted 0.10 μM. The *DL* obtained

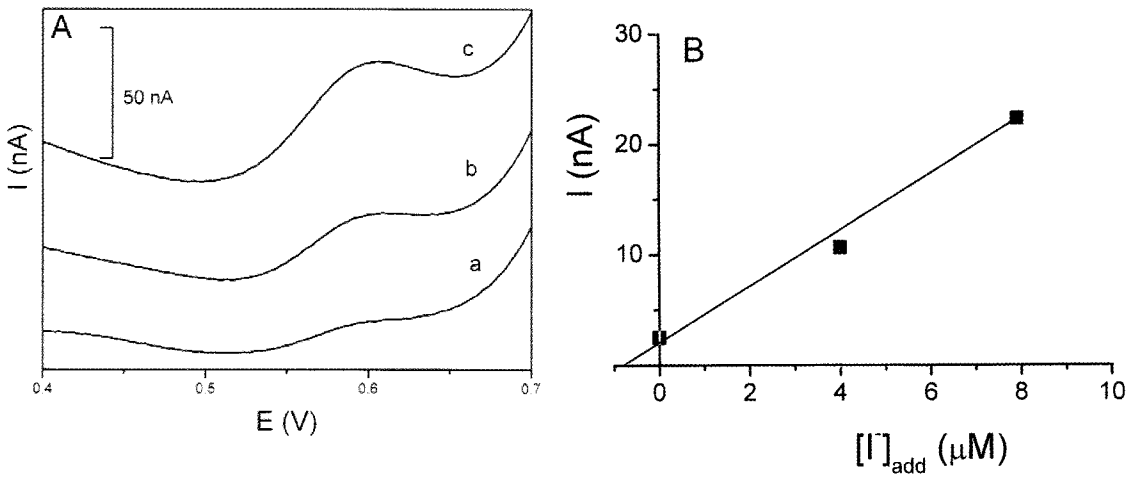

Fig. 4 - A) SWV recorded at a NEE in acidified lagoon water: (a) sample; (b) (c) after standard addition of 4 and 8 μM KI, respectively. Experimental conditions of SWV: pulse height = 50 mV, frequency = 2 Hz. B) Standard addition plot.

by the SWV is indeed three times smaller than the one obtained by the CV. These results confirm the fact that iodide can be determined in lagoon water with NEEs, but the use of the SWV is required to improve *DLs* to values low enough to perform analyses in lagoon waters.

4. Conclusions

Nanoelectrode ensembles are advanced nanotech electrochemical devices which allow the improvement of detection limits in environmental electroanalysis, also as far as samples from the marine environment are concerned.

The preliminary results presented here show that the use of gold NEEs indeed allows, the direct determination of micromolar and even submicromolar concentrations of iodide by simple cyclic voltammetry, in iodized edible salt, without requiring any preceding pre-concentration of the analyte. On the other hand, for the determination of iodide in lagoon water, the detection limit achievable by the CV at NEEs is, perhaps, too close to the expected concentration levels so that the precision of the determination needs to be improved. This can be successfully done in the next future by combining advanced electrode systems, such as NEEs, with highly sensitive electroanalytical techniques such as square wave voltammetry.

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