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GALVANOSTATIC COPPER DEPOSITION ON NANOSTRUCTURED CARBON SCREEN PRINTED ELECTRODES

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ABSTRACT

Galvanostatic copper deposition is studied on two types of screen-printed electrodes (SPEs) coated with carbon nanofibers (CNF) or single-walled carbon nanotubes (SWCNT) in view of possible applications for electrochemical sensing of nitrate ions. It is found that the efficiency of the copper electrodeposition and the number and size of the obtained metal particles depend on the type of the carbon support. By varying the galvanostatic current and time the metal deposition is optimized in view of the use of the Cu-modified SPEs for nitrate reduction in slightly acidic solutions. It is demonstrated that under optimized conditions the Cu-modified CNF SPE shows better electrochemical stability and electroanalytical sensitivity for nitrate reduction than the Cu-modified SWCNT one.

Keywords: electrodeposition, copper, carbon nanofibers, carbon nanotubes, nitrate sensing.

INTRODUCTION

Screen printed electrodes (SPEs) present suitable and versatile platforms for the development of different electrochemical sensing devices. This is due to the possibility to functionalize the electrode surface through a variety of methods including pre- and post-modifications of the basic electrode material [1]. Post-treatments including metal electrodeposition are often used to obtain metal nanoparticles that serve further as electrocatalyst for specific reactions. Copper electrodeposition on carbon SPEs was explored in few cases [2 - 5] in view of electroanalytical determination of aminoacids [2, 4] and sugars [3, 5]. These reactions were studied in alkaline solutions where surface copper oxide is involved in the electrochemical process. In all so far studied cases the obtained electrodes were coated with densely packed Cu particles and the carbon SPEs were meant only as carrying substrates with no further specific role. Optimization with respect to the copper deposit [3, 5] was carried out in view of the respective electroanalytic signal but no studies of the stability of the metal phase upon exposure to the analytes were shown.

Copper is known to be a good electrocatalyst for the reduction of nitrate ions being a promoter of the nitrate to nitrite reduction. The latter is the rate determining step of the electrtochemical reaction in acidic solutions [6]. However, although a good catalyst, Cu is unstable in the presence of oxygen in acidic solutions [7 - 9] and thus careful optimization with respect to the metal deposit and its stability upon exposure to acidic solutions is necessary. The aim of the present study is to find optimal conditions for copper deposition at two types of nanostructured carbon SPEs in view of their application for electrochemical sensing of nitrate ions in slightly acidic solutions. Different copper-modified electrodes [10 - 15] were studied for this aim but carbon SPEs were until recently not addressed. In a former study [16] we have compared the electroanalytical performance of Cu- and Cu-Pd-modified nanostructured carbon SPEs with respect to nitrate reduction. Here we present optimization studies concerning the copper deposition process on carbon nanofibers (CNF) and single walled carbon nanotubes (SWCNT) SPEs.

EXPERIMENTAL

Carbon SPEs, DS-110CNF and DS-110SWCNT (Metrohm-DropSens, Oviedo, Spain) with geometrical surface area of 0.126 cm^2 were used in this study. The electrochemical measurements were carried out by means of an Ivium CompactStat potentiostat/galvanostat (The Netherlands) in three-electrode configuration with an external Ag/AgCl reference electrode and a platinum plate counter electrode. All solutions were de-aerated with argon for at least 10 minutes before electrochemical measurements.

Galvanostatic copper deposition was carried out in an aqueous solution of 0.033 mol L^{-1} $CuSO_4$ and 0.5 mol L^{-1} H_2SO_4 by applying a constant current, -200 µA or -300 µA, for different times. To denote the copper deposition conditions the notation (I/t) is used further with I being the absolute value of the applied current (in µA) and t - the value of the deposition time (in seconds). Thus, the notation (200/20) stays for deposition at -200 µA for 20 s. (The equilibrium potential of copper in the plating solution is $E_{eq}(Cu)_{=}0.08$ V vs Ag/AgCl.) The amount of deposited copper was monitored by anodic stripping voltammetry in 0.5 mol L^{-1} H_2SO_4 at scan rate 5 mV s^{-1}. In the anodic stripping experiments at least two complete voltammetric cycles were measured in order to ensure the complete dissolution of the available metal. The voltammetric stripping peaks were used to calculate the dissolution charge corresponding to the metal obtained in the galvanostatic deposition step.

Nitrate electroreduction was studied by means of linear sweep voltammetry (LSV) at 50 mV s^{-1} in aqueous solution of 0.1 mol L^{-1} Na_2SO_4 and different concentrations of $NaNO_3$. The Na_2SO_4 solution was adjusted to pH 2 or pH 3 by means of sulfuric acid.

Imaging of the Cu-modified SPEs was carried out by means of a Jeol 6390 Scanning Electron Microscope (SEM).

RESULTS AND DISCUSSION

Fig. 1 presents potential transients obtained in the course of galvanostatic deposition at conditions 200/20 and 300/13.3 using CNF and SWCNT SPEs. For both current values the duration of the experiments is chosen in a way to have the same charge, Q_{dep} = 4 mC, passed through the system. The experimentally obtained potential transients are typical for metal nucleation and growth with maxima observed in the short times [17, 18]. The initial rise in overpotential is due to the necessity to drive the nucleation process. Once enough metal nuclei are formed on the electrode substrate the applied current becomes consumed for their growth and the overpotential decreases. Despite this general common trend, there are marked differences in the potential transients depending on type of electrode and applied current density. Thus, higher overpotentials are needed to drive and sustain the copper deposition process on the CNF in comparison to the SWCNT SPEs. This means that both nucleation and growth are inhibited on the former electrode substrates.

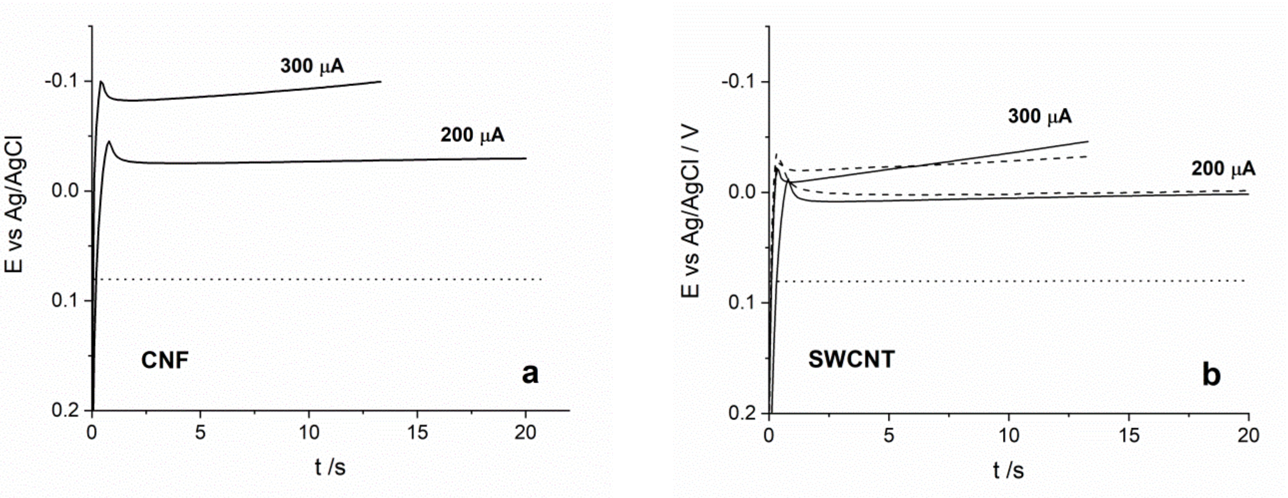

Fig. 1. Potential transients obtained in the course of galvanostatic deposition of Cu at 200/20 and 300/13.3 by using (a) CNF and (b) SWCNT SPEs. Full and dashed lines in plot (b) denote electrodes from different batches. The dotted lines show the equilibrium potential of copper in the plating solution.

This finding should be related to the more than 200 Ω higher resistance of CNF (compared to SWCNT) SPEs, already established in a previous investigation [19]. A further peculiarity of the potential transients is the gradual increase in overpotential observed at the long times, markedly visible at the higher current value (-300 µA) and especially for SWCNT. Such a behavior is rather unusual and indicates to inhibited growth in the advanced stage of the process.

The size and surface distribution of the deposited metal particles was studied by SEM images obtained at different magnifications. Statistical analysis of the images has provided data for the mean size of the metal particles and their size distribution. The comparison of the metal deposit obtained at both types of SPEs at -200 µA (Fig. 2 (a),(b)) shows a lower number of copper crystals for CNF with a somewhat larger mean size, i.e. 0.43 µm for CNF vs 0.40 µm for SWCNT. At the higher deposition current (-300 µA) (Fig. 2 (c),(d)) the number of metal particles on the CNF surface is significantly increased and the mean size amounts to 0.14 µm. In contrast, the SWCNT sample obtained at 300/13.3 (Fig. 2(d)) shows two types of Cu crystals: a large number of circular particles with mean size 0.23 µm and a much lower number of large crystals with mean size of 1.24 µm. The latter are frequently found in macrodefects (cracks) of the substrate and should have appeared first on the electrode surface. Large crystals vertically stuck in the carbon structure may be in the origin of the increasing overpotential observed at long times, especially for the SWCNT substrate, due to the inhibited growth through the small contact area to the underlying substrate.

The amount of deposited copper obtained in the

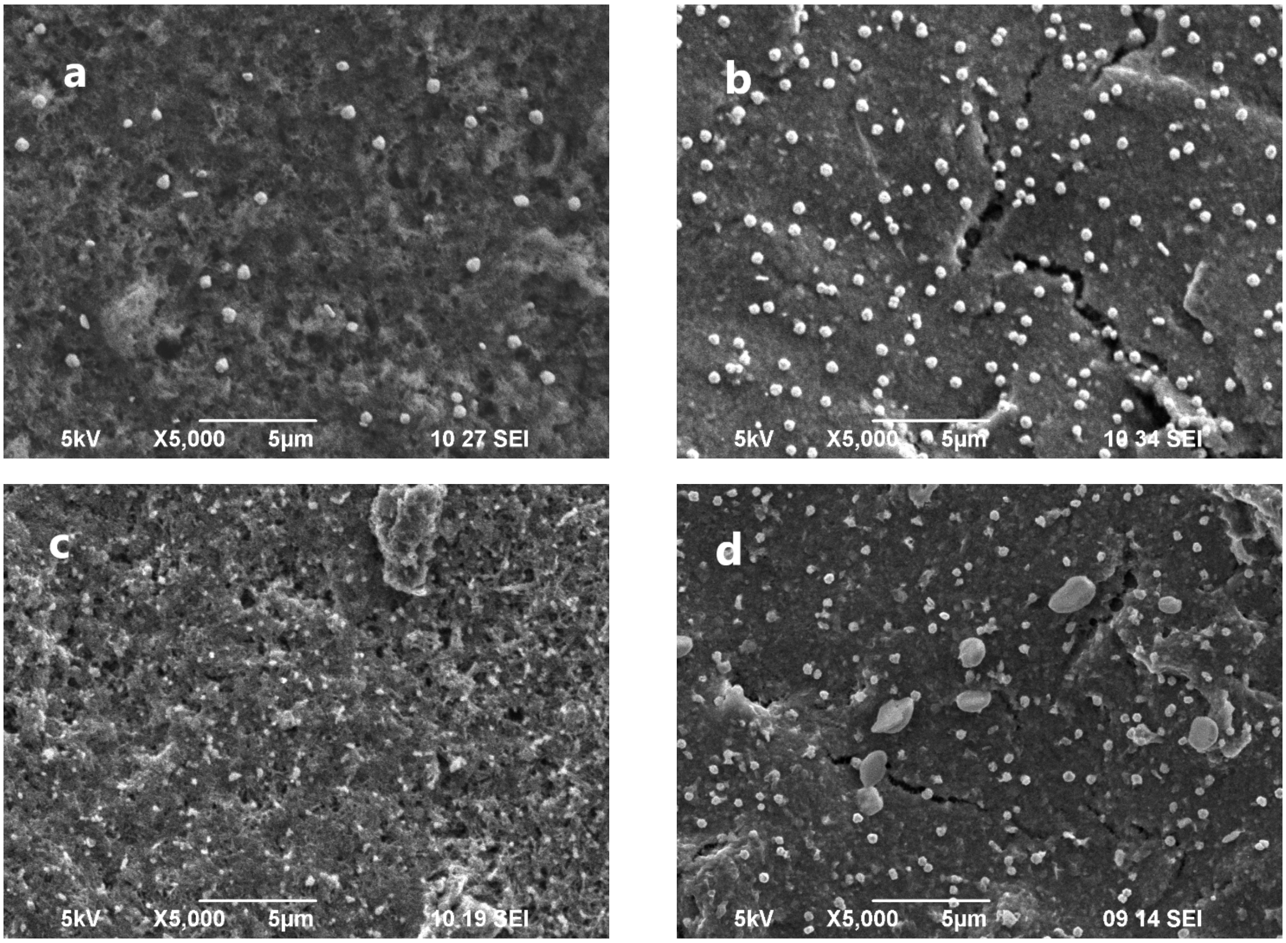

Fig. 2. SEM images obtained at CNF (a,c) and SWCNT (b,d) SPEs after galvanostatic Cu deposition: (a, b) 200/20, and (c,d) 300/13.3.

galvanostatic experiments (Fig.1) was monitored by stripping voltammetry in sulfuric acid (Fig. 3). The charge, Q_{diss}, under the voltammetric peaks was used to calculate the charge deposition efficiency, $CD_{eff} = Q_{diss}/Q_{dep}$ For the CNF electrodes (Fig. 3 a) the voltammetric curves show one and the same amount of deposited copper irrespective of the applied current and CD_{eff} values of about 0.7. The voltammetric stripping curves obtained with SWCNT electrodes (Fig. 3 (b)) correspond to two batches of SWCNT electrodes. The deposition efficiency was largely differing from batch to batch with CD_{eff} values ranging between 0.9 and 0.7 for batch 1 and $CD_{eff} \approx 0.4$ for batch 2. In fact, the Cu^{2+} ions undergo a two-step reduction:

$Cu^{2+} + e^- \rightarrow Cu^+$ (slow)

$Cu^+ + e^- \rightarrow Cu^o$ (fast)

with the discharge of the bivalent to univalent ones, Cu^+ being the rate determining step. Therefore, low values of CD_{eff} should mean that the second electrochemical step is in a way inhibited or slowed down so that diffusion of the Cu^+ ions away from the electrode/electrolyte interface is prevailing instead of occurrence of the second reductive step resulting in growth of the deposited copper particles. As shown in a study of copper electrocrystallisation on glassy carbon electrodes [20] the discharge of copper ions accelerates in the presence of specifically adsorbed anions and oxygen-containing surface groups as those found on the carbon surface. Thus, it seems that the surface functionalization differs largely on SWCNT electrodes from different batches. For that reason, studies on the stability of the Cu-modified SPEs were carried out mainly with CNF SPEs that showed a more reproducible behavior.

The stability of the Cu deposit with respect to nitrate ions reduction was studied in slightly acidic solutions (pH 2 and pH 3) containing 1 mmol L^{-1} nitrate by using CNF electrodes. Cu was deposited at -300 μA for three different times: 13.3 s, 20.0 s and 27.0 s. The LSV measurements obtained at these three Cu-modified electrodes (Fig. 4) show no substantial difference in the nitrate reduction signal depending on the amount of deposited copper, a result that implies a diffusion-limited reaction. The amount of copper obtained after the measurements in nitrate-containing solution were assessed by anodic stripping voltammetry and compared to reference measurement completed without exposing the Cu-modified electrodes to nitrate reduction. One and the same CNF electrode was used for the whole measurement series. The results obtained after the treatment in nitrate at two pH values are presented in Fig. 5. The data show that for all copper deposits the exposure to nitrate leads to a loss of copper which increases with increasing pH. Therefore, pH 2 was identified for further measurements. Concerning the amount of deposited copper, the conditions 300/20 were chosen in order to have larger and in the same time not-overlapping copper particles (Fig. 6).

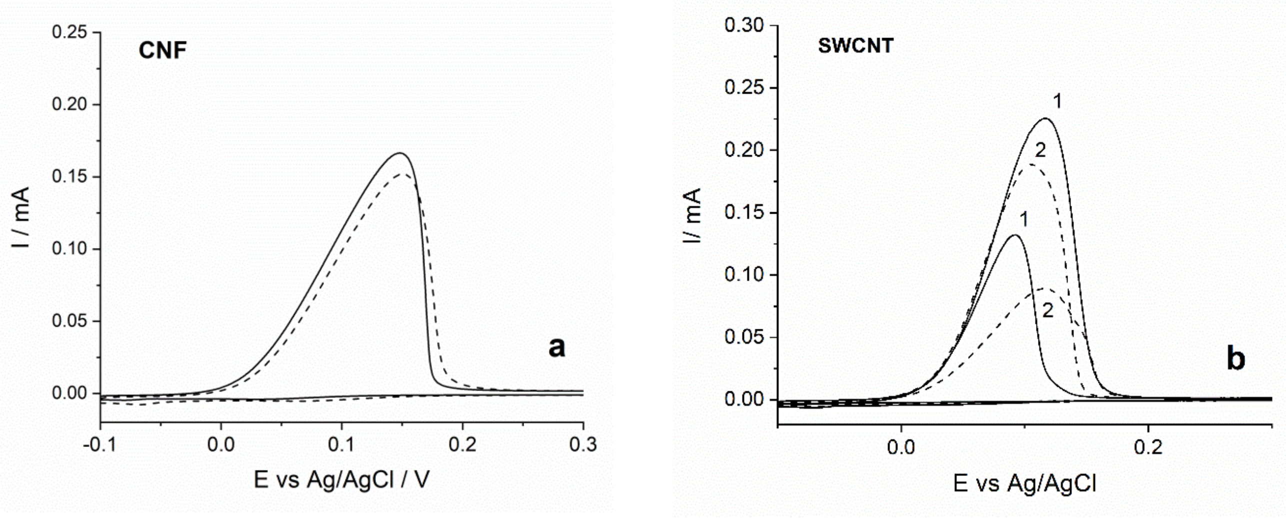

Fig. 3. Anodic stripping curves measured after deposition of Cu, 300/13.3 (full lines) and 200/20 (dashed lines) at (a) CNF and (b) SWCNT SPEs. Numbers in plot (b) denote measurements on electrodes from different batches (1 and 2). Scan rate 5 mV s^{-1}.

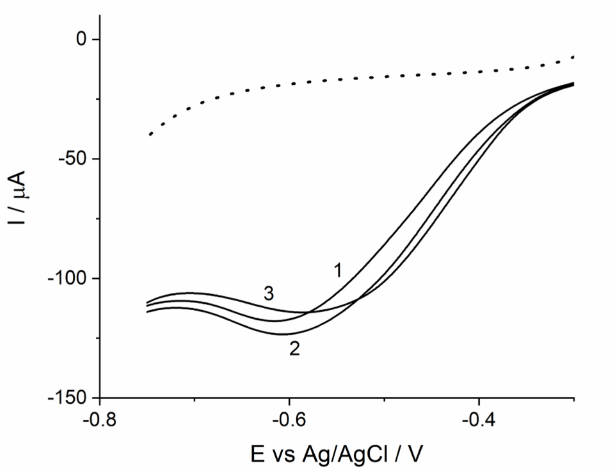

Fig. 4. LSV measurements at 50 mV s^{-1} in aqueous solution of 0.1 mol L^{-1} Na_2SO_4 and 1 mmol L^{-1} $NaNO_3$ (pH 2). Lines 1, 2, and 3 are obtained for Cu deposition on CNF at 300/13.3, 300/20 and 300/27, respectively. The dotted line shows the measurement in the absence of nitrate.

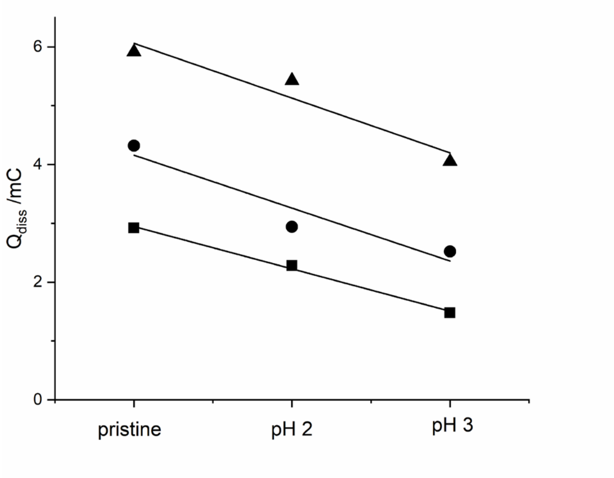

Fig. 5. Data for the dissolution charge without treatment in nitrate solution (pristine) and after treatment in the presence of 1 mmol L^{-1}nitrate ions at two pH values of the 0.1 mol L^{-1} Na_2SO_4 solution (pH 2 and pH 3). CNF SPE with copper deposit obtained at: 300/13.3 (■), 300/20 (●), and 300/27 (▲).

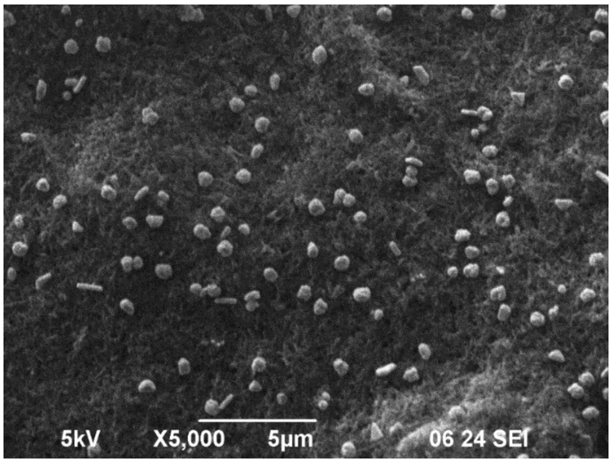

Fig. 6. SEM of copper crystals deposited on CNF electrode at 300/20.

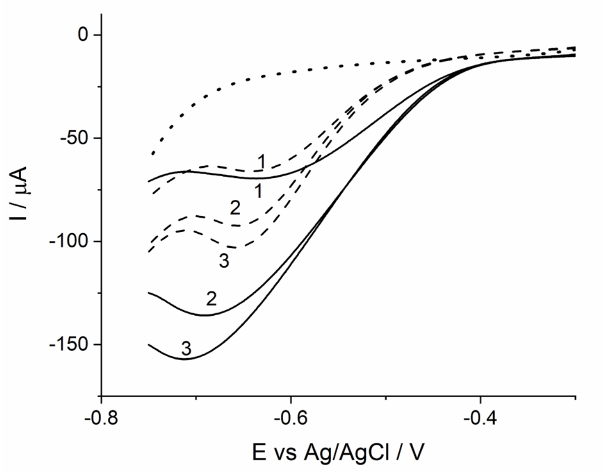

Fig. 7. LSV measured at Cu (300/20)-modified CNF (full lines) and Cu (300/13.3)-modified SWCNT (dashed lines) electrodes in 0.1 mmol L^{-1} Na_2SO_4 and different concentrations of $NaNO_3$: (1) 0.5 mmol L^{-1}, (2) 1.0 mmol L^{-1} and (3) 1.2 mmol L^{-1}. The dotted line shows the measurement in the absence of nitrate ions.

Finally, LSV measurements carried out at three nitrate concentrations by means of Cu(300/20)-modified CNF electrode are shown in Fig. 7 (full lines). The nitrate reduction peaks are well discernable and proportional to the analyte concentration. For comparison, the electroanalytical response of a Cu(300/13.3)-modified SWCNT electrode is also shown in the figure (Fig. 7, dashed lines). A less sensitive LSV response for nitrate reduction and a saturation of the electroanalytical signal starting already at about 1.2 mmol L^{-1} is observed in this case. Bearing in mind that the nitrate reduction reaction is diffusion controlled the established difference in the electroanalytical behavior of both types of carbon SPEs should be related to the different surface state of the nanostructured carbon substrates and their different interaction with the analyte and the products of the reduction reaction.

CONCLUSIONS

The present investigations demonstrate the possibility to influence the type of the copper deposit obtained in galvanostatic mode by using different nanostructured carbon SPEs. The following conclusions may be drawn:

- The use of higher galvanostatic currents results in higher number of deposited crystals with size and size distribution of the metal particles depending markedly on the carbon substrate;
- A narrow size distribution of homogeneously distributed copper particles is obtained in the CNF case whereas the macrodefects of the SWCNT SPEs induce a bi-modal deposition of metal particles with very different mean sizes of the copper crystals;
- In the nitrate reduction studies carried out in slightly acidic solutions (pH 2 and pH 3) a better electrochemical stability of the Cu-modified CNF is found at pH 2;
- Under optimized conditions the Cu-modified CNF SPEs have better electroanalytical sensitivity for nitrate reduction than the Cu-modified SWCNT SPEs;
- The different surface functionalization of both types of carbon substrates results most probably in different surface interactions with the analyte species and the products of the electrochemical reaction.

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