Copper nanowire array as highly selective electrochemical sensor of nitrate ions in water

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Abstract

Contamination of water with nitrate ions is a significant problem that affects many areas of the world. The danger from nitrates is not so much their toxicity, rather low, as their transformation into nitrites and in particular into nitrosamines, substances considered to be a possible carcinogenic risk. For this reason, European legislation has set the maximum permissible concentration of nitrates in drinking water at 44 mg/l. Thus, it is clear that a continuous monitoring of nitrate ions is of high technological interest but it must be rapid, easy to perform and directly performable in situ. Electrochemical detection is certainly among the best techniques to obtain the above requirements. In particular, in this work we have developed a nanostructured sensor based on array of copper nanowires obtained with the simple method of galvanic deposition. The nanostructured sensors have a very short response time with a detection limit less than 10 μM. Different interfering species were tested finding a negligible effect except for the chlorine ions. However, this problem has been solved by removing chlorine ions from the water through a simple precipitation of chloride compounds with low solubility. Nanostructured sensors were also used to analyze real water samples (rain, river and drinking water). In the case of drinking water, we have measured a concentration of nitrate ions very close to the that measured by conventional laboratory techniques.

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1. Introduction

In the last decades, the contamination of water with nitrate ions is of more and more importance. Agricultural and livestock sectors are the main sources of nitrate contamination [1]. In fact, nitrogen-based fertilizers are highly used in agriculture and their over-use leads to a release of nitrate ions directly in ground water with the consequent contamination of the food chain. High nitrate concentration in the aquatic environment leads to the overgrowth of algae causing an oxygen depletion (eutrophication) that is highly harmful for aquatic species [2]. High level of nitrate ions, is also dangerous for human health [3][4] , because they are converted into different harmful nitrogen based compound such as nitrite, nitric oxide, N-nitroso compounds [5,6] that are responsible of several diseases: such as cancer, Parkinson and gastritis [7–9]. More important, nitrate ions are responsible of the blue-baby syndrome (or methemoglobinemia), due to the oxidation of the hemoglobin in methemoblogin by nitrate ions that have a lower capability to oxygen transport [10,11].

For these reasons, the Acceptable Daily Intake (ADI) of nitrate has been imposed at 3.7 mg/kg body-weight by the Food and Agriculture Organization (FAO) of the United Nation (UN) and by the World Health Organization (WHO) in 2002 [4], [7]. Besides, the Environmental Protection Agency (EPA), has established the maximum amount of nitrates ions in drinkable water at 44 mg/L, limit that is also valid in many European countries [12]. Therefore, it is clear that monitoring the ecological concentration of nitrates has gained increasing importance. Many techniques can be used to detect nitrates but generally the choice depends on the sample nature, the expected nitrate concentration and the kind of required analysis (time, in situ). Generally, spectroscopy techniques are the most used because allow to carry out analyses with high precision and reaching low LOD [13]. However, these techniques require skilled workforces and specific

instrumentations, besides the procedure is long and hard (i.e. the conversion of nitrates in nitrites by using cadmium or zinc salts, preparation of standards) [14], [2].

In this context, is clear that the development of an easy, fast and not-lab-depended technology to detect nitrate ions is of great importance and can help the continuously monitoring the pollution of natural water. Electrochemical sensors are perfect candidates to overcome all these limits, being fast, cheap, easy to use and can work with simple and small instrumentations [15–20]. Different type of electrochemical sensors have been exploited in order to quantify nitrates, such as impedimetric [21]; [22], chronoamperometric [23–27], voltammetric [28]; [29–33] and also biosensors [34,35], [36]. As concern the enzymatic biosensors they permit to obtain very low Limit Of Detection (LOD) but the detection is very hard, expensive and time consuming (accurate pH control, many separation and incubation steps) [37]. Many different electrode materials have been tested and studied for nitrate ions detection but, in the last years, researchers have focused on copper based electrodes due to its low overpotential for reduction of nitrate ions [38]. Davis et al. [39] developed a macro-porous copper electrode founding a LOD of about 10 mM. In recent years, this LOD has been decreased by using nanosized copper electrodes. For example, Essousi et al. [40] using a ion imprinted polymer coated with copper NPs have obtained a LOD of about 1000 times lower that is probably due to the high surface area of nanoparticles. Similarly, others authors [41,42] took advantage of the high surface area of copper NPs and the good electrical properties of carbonaceous materials, such as carbon nanotubes and disposable pencil graphite, to detect nitrate in a wide linear range. Interesting is also the approach followed by Wu et al [43] that have prepared Cu nanowire array by electrochemical reduction of copper oxide nanowires obtained by thermal oxidation. Using this electrode and the amperometric detection, have detected nitrate ions in the linear range of 50 μM to 600 μM with a LOD of 12.2 μM.

In this work we have focused our attention on the possibility to use vertically standing copper nanowires (Cu NWs) obtained by template galvanic deposition (GD) into nanoporous

membrane [44], [45]. The overall process is cost effective, scalable, fast and Cu NWs that are well anchored to a copper current collector can be easily obtained. Furthermore, GD process can be used to synthesize different kind of electrode materials, such as nickel [46,47]; [48], palladium [49,50], amorphous silicon [51], compound of lead [52] and so on. Using this kind of nanostructured electrode, the surface area of the sensor is about 70 time higher that bare ones and this is a special property for electrochemical devices that should enhance their performance [18], [53], [16], [54]. Cu nanowires obtained by template electrodeposition were tested by Stortini et al [55] who found very interesting results and obtained a very low LOD. They also demonstrated that the electrode is able to detect nitrate ions in water sample containing interfering chloride ions at low concentration.

Considering the increase of activity of nanostructured copper, in this work we have studied the performance of vertically standing Cu NWs obtained by the simple and low-cost method of GD for nitrate detection in water by using Linear Sweep Voltammetry (LSV). A low LOD of about 9.1 μM, almost 100 times lower than the limit established by EPA and WHO that is about 750 μM (50 ppm), in a wide linear range was found. The effect of many interferences (chlorine, potassium, sodium, sulfate, magnesium, carbonate anions, copper, lead, zinc, aluminum, mercury, nickel) will be also shown and described. Finally, nitrate ions were also successfully detected in real samples (river, rain and drinking water) demonstrating the real applicability of the proposed system.

2. Experimental

Commercial polycarbonate membranes (Poretics^{TM}) were used as template for copper GD. The membrane has a thickness of about 8 μm and consists of interconnected cylindrical pore (Figure S1) with a nominal mean diameter of about 200. Nanowires growth were performed according to previous work [44]. Briefly, one surface of the membrane was sputtered with gold (for 1 minute) in order to make it conductive for the subsequent deposition of copper current collector (about 12 μm thick). This step was carried out at constant current (8 mA/cm^2) for 1 h, in an electrochemical cell containing a Pt mesh as a counter electrode and an aqueous solution of 0.2 M

101 $CuSO_4.5H_2O$ and 0.1 M H_3BO_3 and powered by a PARSTAT galvanostat (mod. 2273). To obtain
102 Cu nanowire by GD, the current collector was electrically coupled with an aluminum tube, by a
103 conductive carbon paste. Aluminum was previously polished with different grade emery paper,
104 washed with distilled water and rinsed ultrasonically in pure acetone. Then, the copper-aluminum
105 couple was immersed in an electrolytic solution containing $CuSO_4$ 0.1M and boric acid 0.05M with
106 pH 2 adjusted by sulfuric acid. This galvanic couple leads to dissolution of aluminum, that acts as
107 sacrificial anode, and the simultaneous deposition of Cu into the polycarbonate pores. After
108 nanowires deposition, samples were etched in pure dichloromethane in order to dissolve the
109 template.

110 Morphology was analyzed by scanning electron microscopy (SEM), using a FEI FEG-
111 ESEM (mod. QUANTA 200) equipped with an Energy Dispersive Spectroscopy (EDS) detector. X-
112 ray diffraction was carried out using a RIGAKU diffractometer (model: D-MAX 25600 HK). All
113 diffraction patterns were obtained in the 2θ range from 10◦ to 100◦ with a step of 0.004◦and a
114 measuring time of 0.067 s for step, using the copper Kα radiation. Diffraction patterns were
115 analyzed by comparison with ICDD database (International Centre for Diffraction Data, card
116 number: Cu 4–836, Au 4–784; AgCl 06–048).

117 For the sensor performance study, nanostructured electrodes were assembled with a copper
118 tape and insulated with a lacquer to have a geometric area of about 0.05 cm^2. Electrochemical tests
119 were carried out in de-aerated (by N_2 purging) aqueous solutions of 0.1 M $NaSO_4$ at different pH
120 (adjusted by sulfuric acid), using a three-electrode cell with Ag/AgCl reference electrode and a Pt
121 mesh as counter electrode. Cyclic voltammetry (CV) was carried out with a scan rate of 50 mV/s in
122 the potential range from −1.4 to -0.1 V vs Ag/AgCl. The effect of solution pH on the sensor
123 performance was studied, by testing different solutions (50 ppm of nitrate). Similarly, the effect of
124 surface area was tested by using electrodes consisting of Cu thin film and Cu-NWs of different
125 length (obtained by chancing the GD time in the range from 30 to 120 minutes). Sensor calibration

curves were obtained by means of LSV carried out in the potential range from -0.1 to -0.8 V (Ag/AgCl) with a scan rate of 10 mV/s, by adding different amount of a standard solution of sodium nitrate to the blank. Selectivity tests were carried out in the presence of copper, lead, nickel, zinc, aluminum, mercury, chorine, potassium, sodium, sulfite, carbonate and magnesium at four different concentrations (0.5, 5, 50 and 500 ppm), in the presence of 50 ppm of nitrate ions. These concentrations are an order of magnitude lower and higher than interfering species, respectively. All the experiments have been repeated at least 3 times.

3. Results and discussion

3.1 Copper nanowire fabrication

The deposition of copper NWs has been carried out by GD. This process can be controlled by adjusted different parameters such as composition and pH of deposition bath, anodic to cathodic area ratio and deposition time [49], [56]. It is a simple process that allows fabrication of nanostructured materials with different morphology like NWs, NTs and NPs [51], [57]. Following the results obtained in our previous work [44] the growth of Cu NWs inside the pore of the template is due to the following reactions:

$$Cu^{2+} + 2e = Cu^{0} \qquad E^{0} = 0.34 \text{ V (NHE)} \qquad (1)$$

$$Al = Al^{3+} + 3e \qquad E^{0} = -1.7 \text{ V (NHE)} \qquad (2)$$

In particular the dissolution of aluminum anode produces the electrons necessary to the reduction of copper ions. This is a spontaneous process that not requires an external power supply, and in fact, the electromotive force of this process ($\xi = E^{0}_{cat} - E^{0}_{an}$) is positive leading to an overall negative Gibbs free energy ($\Delta G = -nF\xi$). Figure 1 shows the SEM images of the as prepared Cu nanowires obtained after a deposition time of 30 min and after template dissolution. The typical morphology of nanowires, consisted of interconnected cylindrical wires, obtainable by template deposition in polycarbonate membrane can be observed [49], [44], [58].

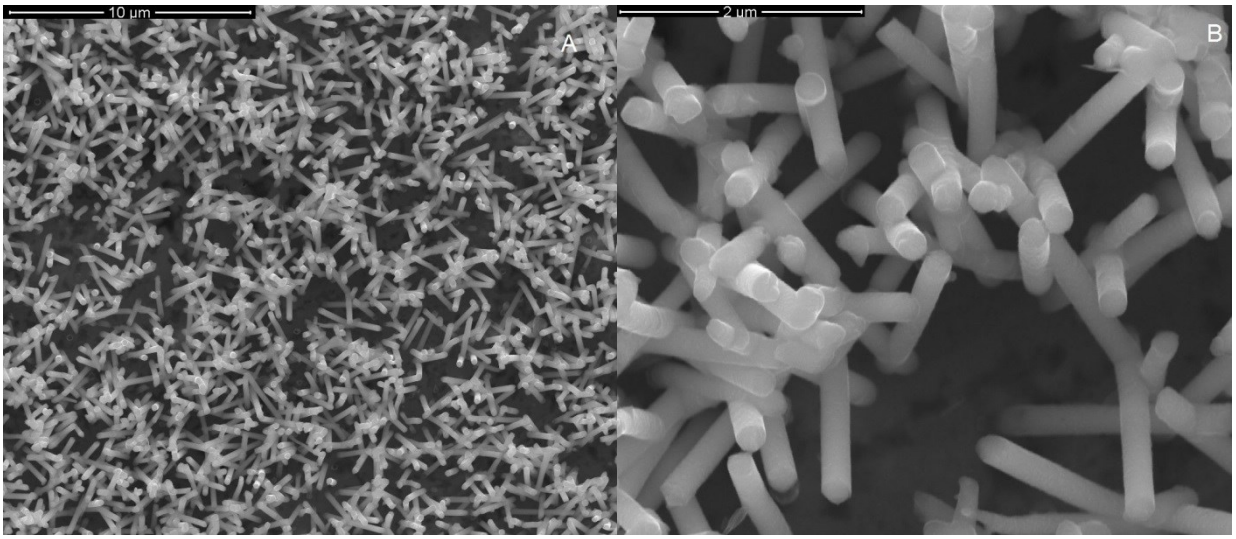


Figure 1 SEM images of Cu-NWs obtained after 30 minutes of deposition

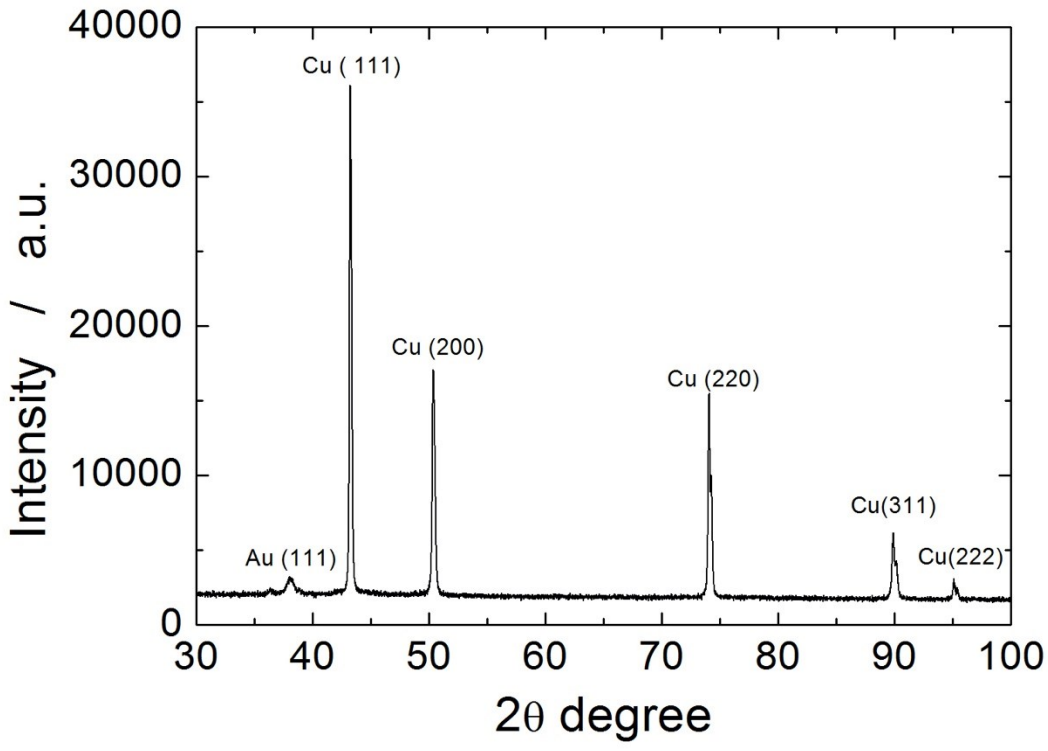


Figure 2 XRD pattern of as-prepared Cu NWs after template dissolution

The NWs length increases with increasing the deposition time, particularly, it moves from 1.38 ± 0.19 µm after 30 min of deposition to 2.65 ± 0.37 µm after 120 min (Figure S2). NWs have

158 an average diameter of about 220 nm (Figure S3a) according to the nominal mean diameter of the
159 pores of polycarbonate template. In order to fully characterize the nanostructured electrode, XRD
160 (Figure 2) and EDS (Figure S3b) analyses were also carried out.

161 By EDS analysis (Figure S3-b), the presence of copper, arising from both the NWs and current
162 collector, sputtered gold and trace of carbon and oxygen due to residual polycarbonate, was found.
163 Figure 2 shows the XRD pattern of the Cu-NWs electrode and the peaks correspond to a cubic
164 phase of copper can be observed. Also, the main peak of gold, from sputtered gold, was identified.
165 Similar XRD patterns and EDS spectra were obtained for all samples regardless of the deposition
166 time. Thus, from these results it is possible to conclude that GD process led to the formation of pure
167 copper nanowires with a polycrystalline structure.

168 ***3.2 Electrochemical tests: optimization and calibration***

169 Electrochemical reduction of nitrate ions involves different redox reactions. Davis et al. [39], using
170 a copper based electrode to detect nitrates and nitrites, have found a peak at about -0.46 V Ag/AgCl
171 that is imputable to the reduction of nitrate to nitrite. A similar result was found by other researchers
172 [59–61]. Other studies found a second peak at more cathodic potential (about -0.86 V Ag/AgCl)
173 that was ascribed to the reduction of nitrate ions to ammonia [62,63]. Starting from these literature
174 data, CV analyses were carried out using the as prepared Cu NWs as working electrode using the
175 blank solution (Na_2SO_4 0.1M at pH 2.5) added with $NaNO_3$ 1mM (Figure 3). The CV curves of
176 Figure 3 shows the presence of both the reduction peaks (at about -0.97 V and -0.42 V Ag/AgCl)
177 above described. The peak at -0.42 V has the higher intensity and so sensors were calibrated using
178 this reduction peak.

179 In order to maximize the peak current, the effect of pH of the detection solution was
180 checked. In fact, pH is a crucial parameter to preserve copper metal from oxidation [64] that would
181 result a short life time of Cu based electrode. To overcome this problem, the use of acidic media is

strongly recommended [24]; [65]; [66]. But, considering that at low pH also the parasitic reaction of hydrogen evolution occurs, it is necessary to find the best value.

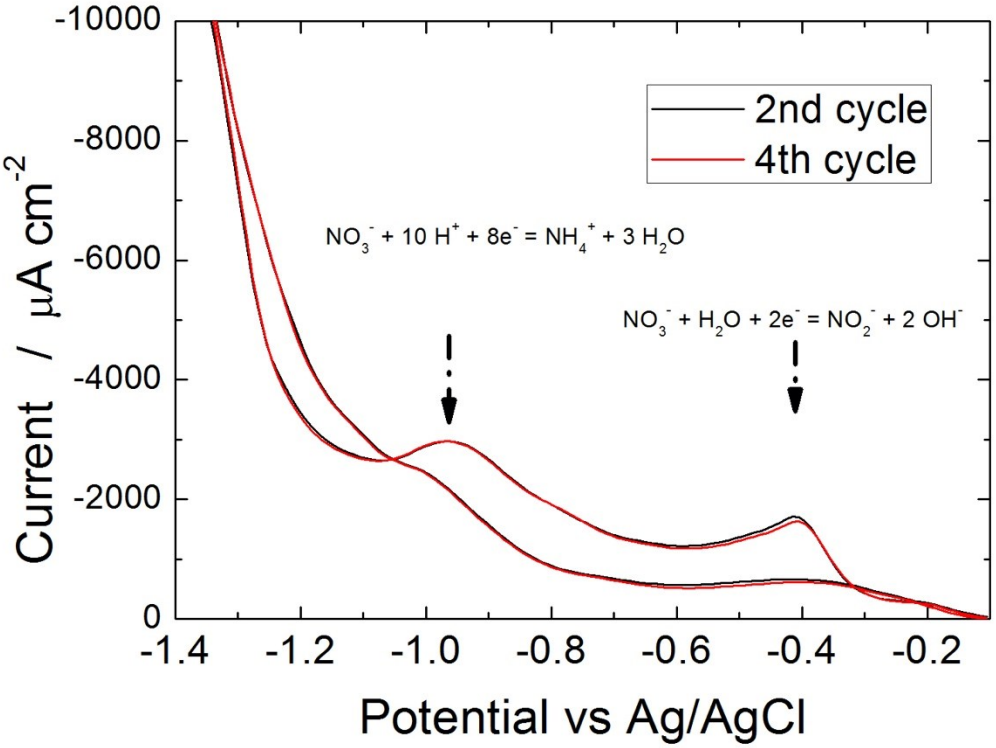
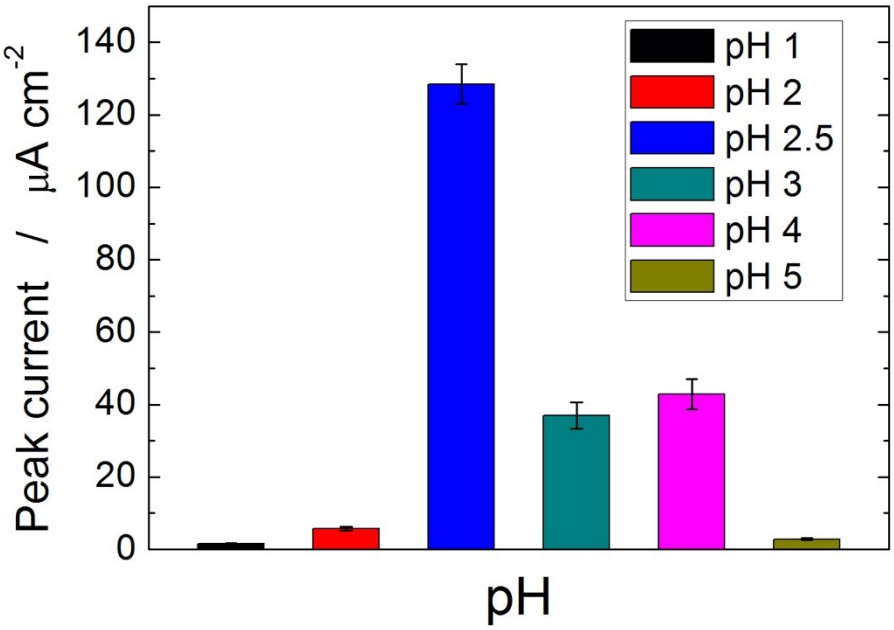


Figure 3 CV in the presence of 1mM of nitrate ions using Cu NWs electrode

Figure 4, shows the effect of pH on the peak current of 3.5 ppm of nitrate using the Cu NWs electrodes. When using a testing solution at pH ≥ 3 the copper electrode changes its color after few analyses, shifting from a pink color to a darker one, indicating the copper oxidation, this led to the decrease of peak current clearly observable in figure 4. For pH ≥ 5 the oxidation phenomena almost completely hindered the detection of nitrate ions. The detection at pH ≤ 2 is minimal due to the presence of hydrogen evolution reaction. The best pH value that we have found is 2.5 that lead to obtain a maximum peak current (130 µA cm^{-2}).



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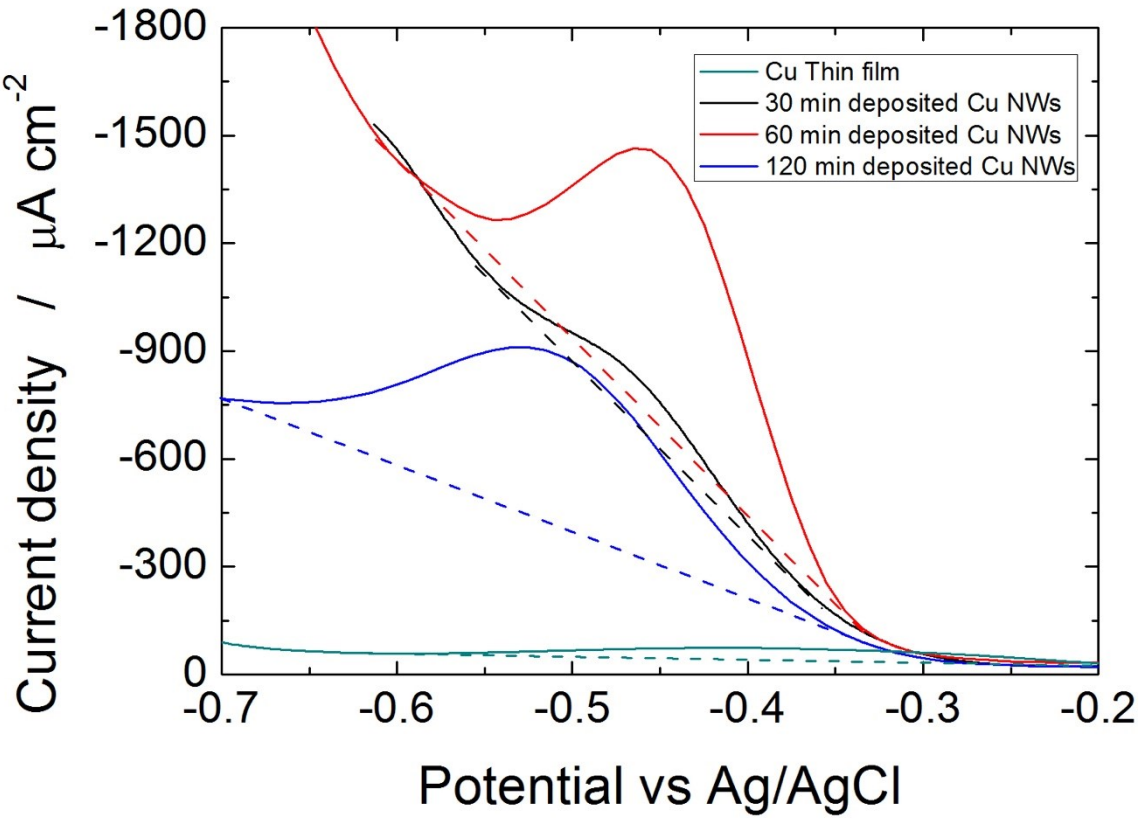
196 **Figure 4** Effect of solution pH on the peak current of the detection of 3.5 ppm of nitrate ions



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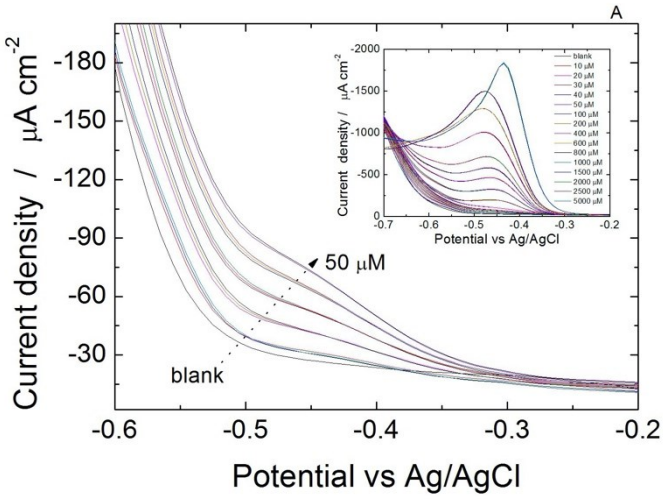
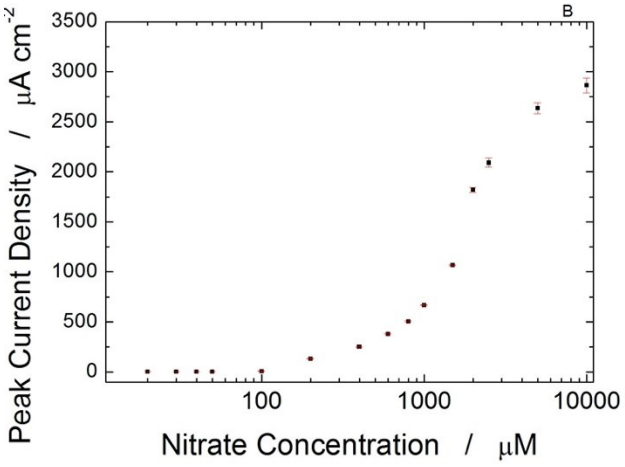
198 **Figure 5** Effect of nanostructures length on the intensity of peak current of nitrate ions detection

Figure 5 shows the effect of NWs length on the peak current of 1mM nitrates in a solution of Na_2SO_4 0.1M at pH 2.5. For comparison, also a copper thin film was tested. From a planar electrode to a nanostructured one, the peak current highly increases due to the increase in surface area. If the NWs length is increased (by increasing the deposition time) from 30 min to 60 min the peak current increased as well, showing again the associated effect of the surface area. Interestingly, if the detection of nitrate ions is tried with longer NWs (120 min of deposition), the peak current decreases. We think that this is an effect of wettability. Indeed, vertically standing NWs are quite hydrophobic [67] and the hydrophobicity increases with increasing NW length. Furthermore, this effect is of importance when using polycarbonate as template because these membranes have many pores interconnections. These pores interconnections decrease the NWs wettability due to a higher physical obstruction. We found that in Poretics polycarbonate template (Figure S1), several interconnections are present, at different points of the cross-section of membrane, mainly located between 2 (from the bottom) and 5 μm. Therefore, nanowires that have lengths close to interconnections, such as those obtained after 120 minutes of deposition, even if they are longer than those obtained with a shorter deposition time, do not exhibit a real increase in the surface area. As is clearly visible in Figure S2, these nanowires have a more compact structure. In fact, as the height increases, the empty spaces between the nanowires decrease, making the structure more and more hydrophobic [68]. These results agree with the results of Figure 5 and justify the decrease in peak intensity.

The effect of increasing nitrate concentration is shown in Figure 6a. In order to show, at the same time, the reproducibility of the sensor, the LSV curves recorded at increasing concentration, from 10 to 50 μM, were repeated in triplicate. For the same concentration value, the LSV curves are almost superimposed (independently of the concentration value) on each other. Thus, it can be concluded, that the electrodes are highly reproducible with a standard deviation of about 7%. The inset of Figure 6a shows the LSV curves for concentration from 100 to 5000 μM. In Figure 6b the

corresponding calibration curve, in the entire investigated concentration range, is reported. As can be see, the shape of the calibration curve is a sigmoid with two identifiable linear ranges, the first with low sensitivity (0.063 μA cm^{-2}, Figure 4c) and a the second with higher sensitivity (0.73 μA cm^{-2}), Figure 4d). After, a final saturation range can be also foreseen. Fernandez-Ramos et al, found a similar behavior when developing a photometric sensor for nitrates [69]. By the way, this is a common behavior of chemical, optical [70–72] and electrochemical sensors [73–77].





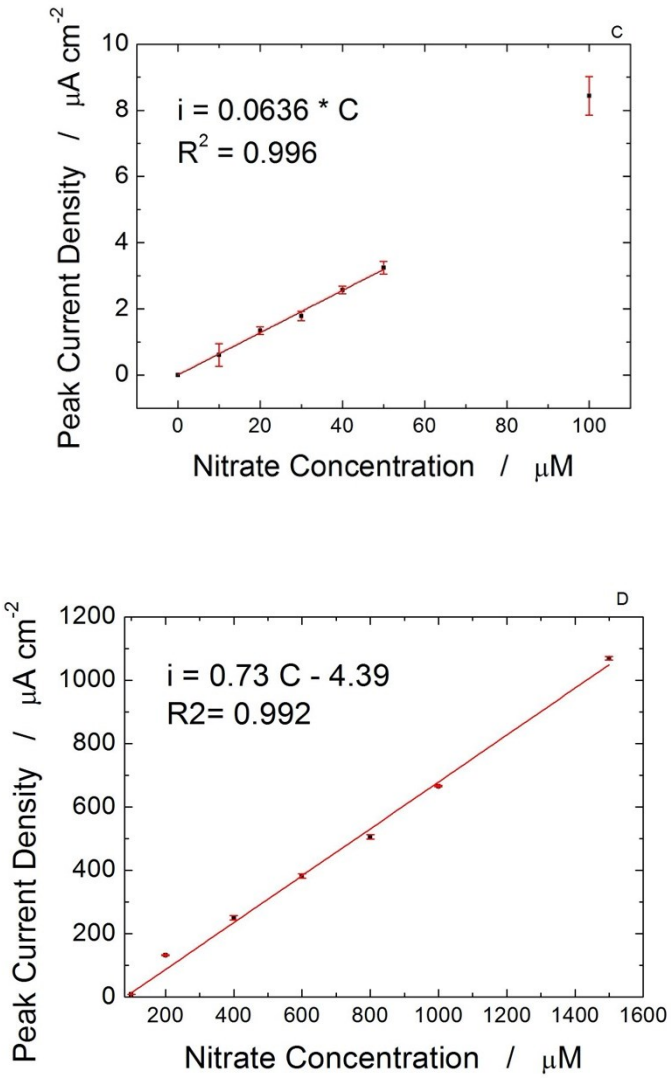


Figure 6 Effect of increasing nitrate ions concentration using Cu NWs electrode obtained with 60 min of galvanic deposition

The LOD was calculated using the following equation:

$$LOD = 3.3 * SD / S \quad (3)$$

where SD is the standard error of the blank and S the sensitivity of the first linear range. The calculated LOD is 9.1 µM, that is comparable to value reported in the literatures (see Table S1, where the performance of most recent electrochemical sensors for nitrate ions detection were listed). A lower LOD was found by [78] using unsorted thermal annealed Cu nanowires and by Stortini et al. [55] using ordered electrodeposited nanowire array. In both approaches, differential

pulse voltammetry (DPV) was employed as detection technique. DPV is a more precise electrochemical method but, in comparison to LSV, it is also more complex to optimize in terms of parameters (length of pulse, time duration, ecc) [79]. It is important to note that the LOD here obtained herein, is much lower than the limits established by EPA and WHO (750 μM) and thus higher precision of sensors is useful but not essential. In addition, our electrodes were made with a very low-cost technique, rapidly and without any expensive post-treatment, such as the annealing at high temperature.

3.3 Interference study

In order to fully determine the performance of an electrochemical sensor, it is of great importance to undertake an interference study. It is well known that the presence of other chemicals can interfere with the detection due to both electrode modification and/or for possible voltametric peaks overlapping. Since the aim of this work is to detect nitrates in water real samples, the interfering chemical species (calcium, magnesium, potassium, chlorine, heavy metals, carbonate ions) were chosen as they typically present in water. These chemicals were added to the testing solution at different concentrations (in a very wide range from 0.5 to 500 ppm) and the results are shown in Figure 7a. In a solution of 50 ppm of nitrates, the addition of 500 ppm of interference species (Mg^{2+}, CO_3^{--}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Hg^{2+}, Al^{3+}, SO_4^{--}, Na^{+}) causes a negligible effect. In fact, the peak current density measured in the presence of the only nitrate ions exhibited a variation of lower than 5%. Among the investigated interfering chemical species, the higher interference comes from carbonate ions (about 5%). Finally, it is important to highlight that is very unusual to find 500 ppm of these chemical species in real water samples.

A considerable interference effect was found when trying to detect nitrates in presence of chlorine ions. This behavior is consistent with literature data [39,65,66,80] and is probably due to the fouling of sensor surface because of the formation of a thin layer of copper chloride [81]. In fact, it was found that as little as 10 ppm of Cl^- decreases the peak intensity of nitrates by about 10% and peak

intensity continued to decrease with increasing Cl^- concentration. This is thus a serious problem for detection of nitrates in real samples, because chlorine ions are always present in water. In particular, chlorine concentration is more than 10,000 ppm in sea water, among 50 and 450 ppm in river water and about 10 ppm in drinking water [81] . In order to overcome this problem, chlorine ions must be removed. A simple method to remove chlorine is the addition of a silver compound into the solution to form silver chloride (among the chlorine compounds it is the one with very low solubility). In fact, the solubility of AgCl is lower than 0.1 ppm [85] and therefore if an appropriate amount of a silver compound (as Ag_2SO_4) is added to the solution, its chemical precipitation occurs. By adding silver sulphate, we have obtained a purple precipitate, that was exanimated by XRD and EDS (Figure S4), confirming the chemical composition of AgCl. It is important to highlight that, due to the solubility of silver sulfate (15 mM [85]), this compound can be used to precipitate up to 1000 ppm of chlorine. If the testing solution contains higher concentration of chlorine (as the sea water), the procedure has to be slightly modified by first adding lead carbonate, in order to precipitate $PbCl_2$. Since the solubility of lead chloride is about 1000 ppm, after its precipitation, it is possible to eliminate the remaining part of chlorine by adding silver sulfate. The possibility that traces of silver or lead ions contaminant the samples to test is not a problem because (as showed in Figure S5 for silver, and in Figure 7 for lead) their presence influences very little the detection of nitrate ions.

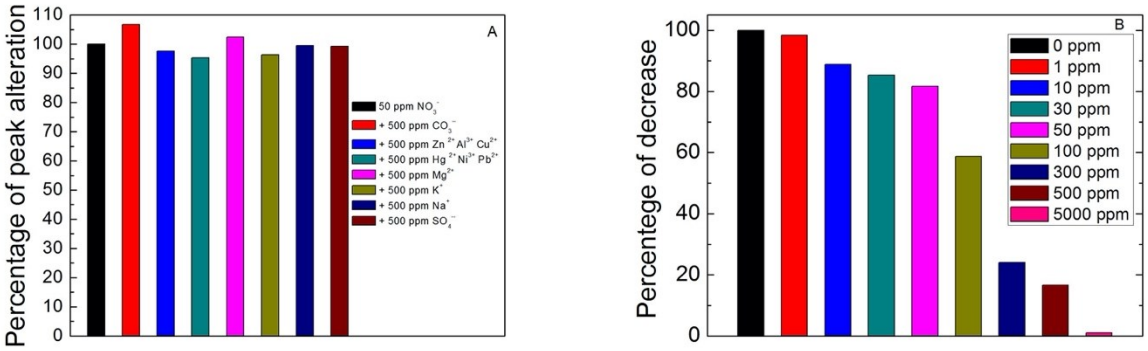
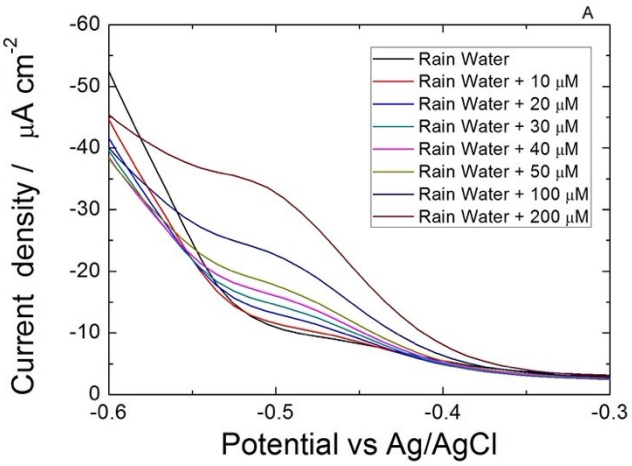
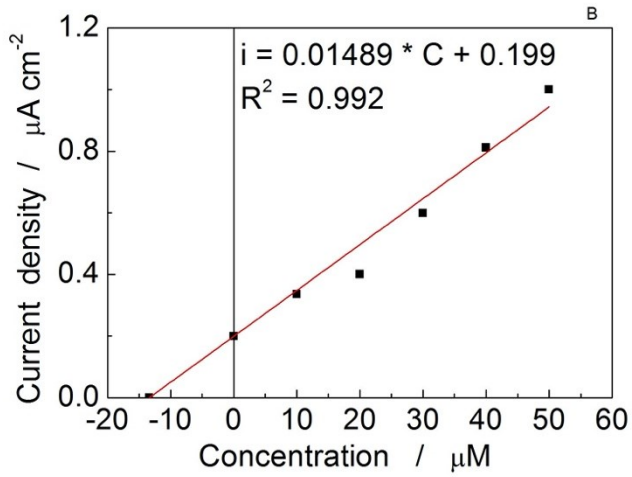


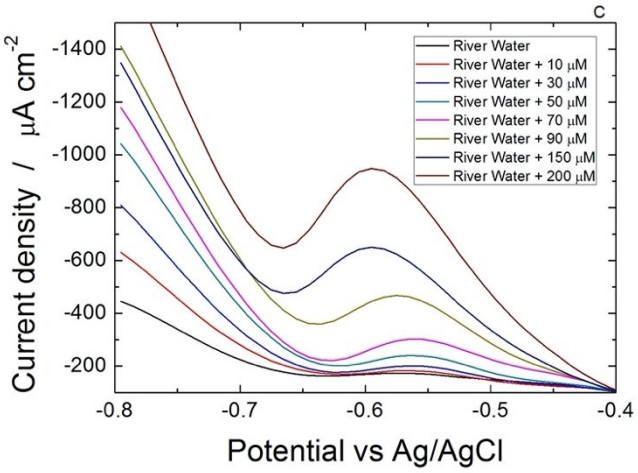
Figure 7 (a) Interference of 500 ppm of different chemical species (b) interference of chlorine on the peak current for the detection of 50 ppm of nitrate ions

3.4 Real sample analysis

In order to validate the sensors with real sample, 3 different water samples were tested: rain water (Figure 8), river water (from Oreto River, Palermo, Sicily, Italy) and drinking water (Italy, commercial water). The method used to quantify the nitrate concentration is the standard addition method (SAM). Using this technique, no calibration lines are needed because it takes into account the effect of the matrix [86,87].







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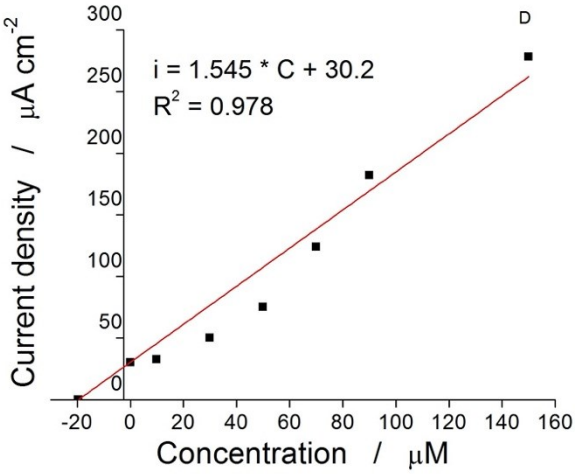

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300 **Figure 8** Real samples analysis. (a-b) Rain water (c-d) water from Oreto river.

301

302 Figure 8a shows the analysis carried out using rain water and the effect of increasing concentration
303 of nitrates. Using the standard addition method (Figure 8b), a nitrate concentration of about 12 μM
304 (0.7 ppm) was detected using equation 3. Water from Oreto river was collected and filtered through
305 paper filter and then acidified using sulfuric acid. If this water sample is tested without any other
306 purification step, no results in terms of nitrates detection are obtained. In fact, using a standard
307 sodium nitrate solution, the peak of reduction of nitrate ions was not detected even at high
308 concentration (up to 5 mM), probably due to the high content of chlorine in this real sample (Figure
309 S6). Thus, water from Oreto was treated by adding silver sulfate in order to remove the chlorine
310 ions. In particular, silver sulfate was added in different steps (for each step an amount of Ag_2SO_4 to

reach a 0.1 mM was used) until to obtain the conclusion of the precipitation of AgCl. After this chemical treatment, the sample was tested and the results are shown in Figure 7b. The chemical purification makes possible the nitrate detection and we found that the peak current increases when increasing the nitrate concentration (Figure 8c). Using the SAM, a concentration of about 22 μM (1.4 ppm) was detected (Figure 8d).

Finally, we have also analyzed samples of drinking water (Italy, commercial water). In this case, since the composition of water is completely known (in Figure S7 the data -sheet of water was reported), these water samples were directly tested and, using the calibration line, we have calculated, from the intensity of the peak current (Figure 9), the corresponding concentration of nitrate ions. The LSV experiment leads to a peak current of about 4.5 μA cm^{-2}, corresponding to 4.38 ppm of nitrate ions (calibration of figure 6C). This value is very close to the value reported in the data-sheet of this commercial drinking water (4.4 ppm, Figure S5) that was measured by conventional laboratory techniques. This result testifying the good behavior of the sensors proposed in this work.

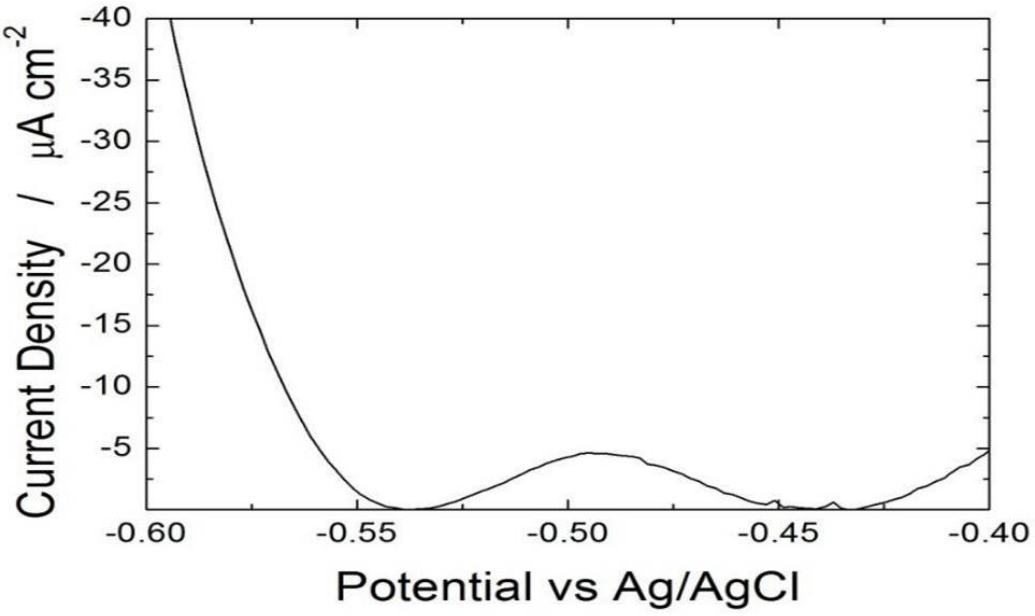

Figure 9 LSV experiment carried out with commercial drinking water

Conclusion

Copper NWs was fabricated by galvanic deposition and successfully used as nitrates sensor. The use of galvanic method makes the electrode fabrication cheap, fast, reproducible and easy to carry out. The NWs length can be controlled by tuning the deposition time and the effect of surface area on the features of nitrates sensor is shown. The sensor was optimized in terms NWs length and pH of solution detection. In the best conditions a LOD of about 9 μM was found. Two linear ranges were found, from 10 to 50 uM and 50 to 1500 μM, with a sensitivity of 0.0636 and 0.73 $\mu A\ \mu M^{-1}\ cm^{-2}$, respectively. Selectivity tests showed that the sensor is highly selective towards many chemical species, typical present in real water samples, but as aspect, the presence of chlorine ions interferes with nitrates detection even at low concentration. In order to overcome this problem an easy and fast procedure is described to make chlorine precipitate. The sensor was validated using real water sample such as rain, river and drinkable water showing the applicability of the proposed electrode.

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Figure Captions

Figure 8 SEM images of Cu-NWs obtained after 30 minutes of deposition

Figure 9 XRD pattern of as-prepared Cu NWs after template dissolution

Figure 10 CV in the presence of 1mM of nitrate ions using Cu NWs electrode

Figure 11 Effect of solution pH on the peak current relative to the detection of 3.5 ppm of nitrate ions

Figure 12 Effect of nanostructures length on the intensity of peak current of nitrate ions detection

Figure 13 Effect of increasing nitrate ions concentration using Cu NWs electrode obtained with 60 min of galvanic deposition

Figure 14 (a) Interference of 500 ppm of different chemical species (b) interference of chlorine on the peak current for the detection of 50 ppm of nitrate ions

Figure 8 Real samples analysis. (a-b) Rain water (c-d) water from Oreto river.

Figure 9 LSV experiment carried out with commercial drinking water