SYNTHESIS OF COPPER NANOWIRES USING AQUEOUS AND IONIC LIQUID ELECTROLYTES FOR ELECTROCHEMICAL DETECTION

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Cu nanowires are particularly attractive due to their catalytic ability and availability representing suitable materials for electrochemical detection of several analytes, including glucose. Herein, Cu nanowires using template-assisted method are developed, involving aqueous solution and ionic liquid based on eutectic mixture of choline chloride with ethylene glycol. Homogeneously distributed ensembles of Cu nanowires have been prepared, having lengths in the range 3-18 μm, depending on the involved electrolyte and applied cathodic potential. The XRD analysis showed that the nature of the electrolyte may influence the preferred crystallographic orientation of the nanowires. Preliminary results suggested that the synthesized Cu nanowire electrodes may act as electrochemical sensing element for enzyme-free amperometric detection of glucose.

Keywords: template-assisted electrodeposition, Cu nanowires, deep eutectic solvents, glucose electrochemical sensing

1. Introduction

In the last decade a significant amount of research has been focused on the synthesis and application of nanoscale materials due to their properties which can be different as compared to their bulk counterpart [1]. A large plethora of nanomaterials possessing different nano-shapes and sizes are currently produced, of which 1-D structures (i.e. nanowires, nanotubes, nanorods) are important for nanotechnology, as they are largely involved to build applications related to nano-electronics, opto-electronics, coatings and sensors [1-5]. Metallic and polymeric nanowires are the most relevant. The metallic nanowires (NWs) usually have diameters from a few nm to 500 nm and have lengths in the range of few μm up to

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tens of μm. The NWs can be quite easily designed and fabricated in various combinations which may add controlled functionality thanks to their geometry.

Metallic NWs may be fabricated involving different techniques, including template-assisted electrodeposition [6-8], chemical methods [9-11] or chemical-vapor deposition [12,13]. Template-assisted electrodeposition has attracted considerable attention, mainly due to the possibility of controlling the length, diameter and density of the fabricated NWs by varying the deposition parameters or the template nature in a simple protocol without the need for complex equipment [6-8, 14]. In addition, their large surface areas and high order allow higher sensitivity and faster response when applied for sensing [14 and included references].

Template electrochemical synthesis represents an elegant approach for the fabrication of nanowires. Arrays of nanowires are obtained by filling the porous template consisting of a large number of straight cylindrical holes with a narrow size distribution, using electrochemical deposition. During the template-assisted electrodeposition of NWs the chemical stability and mechanical characteristics of the template, as well as the diameter, uniformity and density of the pores should be considered. Usually, anodic alumina membranes, polycarbonate membranes (simple or track-etched) and nanochannel array glass or mesoporous channel hosts are mostly involved to electrochemically production of NWs [15-17].

Cu based nanowires are particularly attractive due to their catalytic ability and ready availability representing suitable materials for electrochemical detection of several analytes, including glucose, hydrogen peroxide and more recently nitrate [18-22]. Moreover, the Cu NWs have been reported to be highly sensitive to glucose oxidation due to an excellent electron transfer along one-dimensional direction [23,24]. Most of the studies have been focused on the use of Cu NWs synthesized through chemical and hydrothermal routes [15,20,21,25] or on the involvement of various Cu nanostructures, including coral-like copper micro-/nano-structures [26] or copper bifacial nanowire arrays [27]. It is worth to mention in this point that the use of templated based electrochemical synthesis of NWs allows a precise control over the size, shape and configuration, as well as growth direction, thus facilitating the preparation of ordered ensembles of Cu NWs, too [22,27].

In this study, preliminary experimental results regarding the template-assisted electrochemical synthesis of Cu nanowires are presented, using as electrolytes both aqueous solutions and ionic liquids based on eutectic mixtures of choline chloride with ethylene glycol (the so-called “deep eutectic solvents” - DES). The as-prepared sensing electrodes without further processing showed clearly an appropriate response towards the electrochemical nonenzymatic glucose detection.

2. Experimental

All used chemical reagents were of p.a. quality (Aldrich) and have been used without any additional purification. Commercial polycarbonate membranes (Whatman, 47 mm disk diameter) (denoted PC) with pore diameter between 80-400 nm were used as template for the electrochemical synthesis of copper nanowires. Because the membrane is not electrically conductive, prior to the electrodeposition process, one of its face has been coated with a thin layer of gold or copper by sputtering or thermal evaporation. This metallized side will act as a cathode for the subsequent electrochemical deposition and also as a stable support for the built nanostructure. The as-prepared membrane was fixed onto a metallic copper tape and an inert material (e.g. chemically resistant paper adhesive tape) was used to cover the surface leaving exposed to electrolyte a disk with a constant geometrical area of 0.2826 cm^2.

Before mounting into the electrochemical cell, the assembled membrane (as working electrode, WE) was immersed in deionized water under ultrasonic stirring for 5 min. To achieve a uniform growth of NWs within the pores, before the electrodeposition process this assembled PC membrane was immersed in the electrolyte for 15 minutes to allow the incorporation of the electrolyte in the pores. The electroplating step was performed using a PARSTAT 4000 potentiostat in a glass cell, against a Pt plate as counterelectrode. Ag/AgCl electrode was used as reference for the applied potential. The Cu NWs growth in pores has been performed involving either aqueous electrolytes or ionic liquids based on eutectic mixtures of choline chloride with ethylene glycol. The composition and working temperature are shown in Table 1.

Table 1

Electrolytes composition and operating parameters

Electrolyte composition	Temperature, °C
0.8 M $CuSO_4$ + 0.6 M H_2SO_4 (aqueous)	25-27
0.8 M $CuSO_4$ + 0.6 M H_2SO_4 + 4 $mL.L^{-1}$ wetting agent (aqueous)	25-27
0.4 M $CuCl_2$ dissolved in ILEG (DES) (ILEG = choline chloride : ethylene glycol, 1:2 molar ratio)	65

In order to measure the diameter and the length of the obtained nanowires, at the end of the electrochemical growth the samples were etched in pure dichloromethane at room temperature (three times, each for 20 min using fresh organic solvent) to remove the membrane template. Then they were rinsed in isopropilic alcohol and ethanol.

The morphology and elemental composition of the Cu NWs have been examined using scanning electron microscopy (SEM) associated with energy dispersive X-ray spectroscopy (EDX) (SU8230, HITACHI High-Technologies Corp.). The phase composition and structure were determined involving X-ray diffractometry (XRD) (High Resolution SmartLab X-ray diffractometer Rigaku, 9 kW, with rotating anode) using CuKα radiation, at a speed of 2 s/step (1step = 0.05^{o}). The electrochemical characterization through cyclic voltammetry and chronoamperometry has been performed using the same PARSTAT 4000 potentiostat in a three-electrode cell containing assembled PC membrane as working electrode, Pt strip as the counter and either Ag/AgCl or Ag wire as reference electrodes. The detection of glucose oxidation on the Cu NWs working electrode in 0.05 M NaOH solution was investigated by cyclic voltammetry (CV) and chronoamperometry.

3. Results and discussion

3.1. Electrochemical synthesis of Cu NWs involving aqueous acidic electrolytes containing $CuSO_4$

Initially, cyclic voltammograms were recorded in order to select the cathodic region suitable for the electrochemical growth of Cu NWs, as exemplified in Fig. 1.

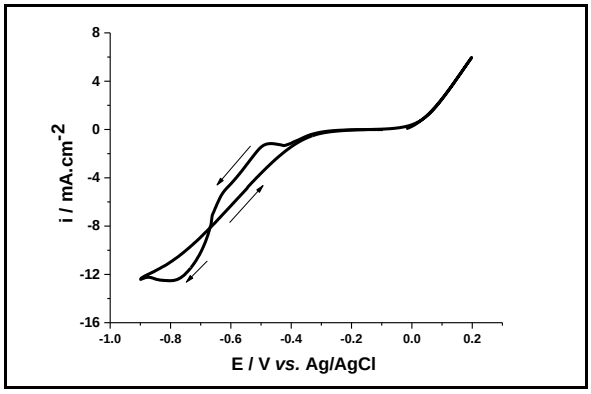


Fig. 1. Cyclic voltammogram of Cu^{2+}/Cu^{o} process from 0.8 M $CuSO_4$ + 0.6 M H_2SO_4 on Au sputtered PC membrane as WE (the scan was started at 0.012 V) and the scan rate was 20 mV s^{-1})

To investigate the influence of the applied cathodic potential on the geometrical characteristics of the prepared Cu NWs, several specimens obtained in the same electrolyte at various values of the potential have been subjected to SEM analysis, as presented in Fig. 2, where the cathodic branch of cyclic voltammogram was represented, too.

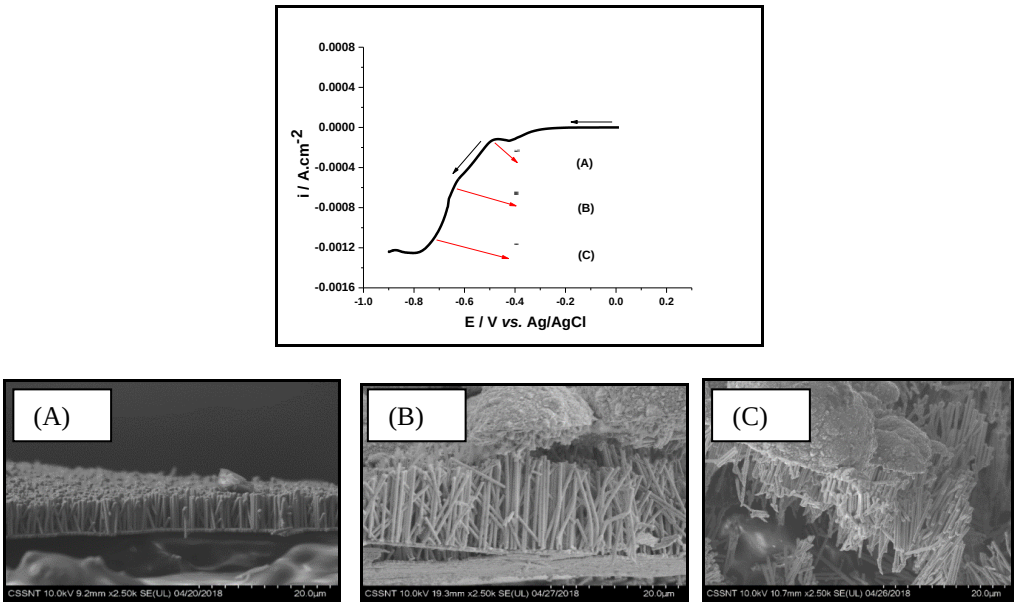


Fig. 2. The influence of the applied cathodic potential on the deposition of copper nanowires from 0.8 M $CuSO_4$ + 0.6 M H_2SO_4 solution: top –the voltammetric curve; (A-C) SEM micrographs at different potential values

As the applied cathodic potential is in the limiting current region, around -0.4 V in this case, the membrane pores are almost filled with copper nanowires (see Fig. 2A). Further displacement of the potential towards more negative values determines the complete filling of the pores and random appearance of several surface regions exhibiting hemispherical caps which then tend to cover entirely the membrane surface (see Fig. 2B and Fig. 2C for samples obtained at about -0.6 V, respectively at ~ -0.75 V). Therefore, an applied cathodic potential in the range of -0.4 ÷ -0.45 V associated to the cathodic limiting current domain should be considered adequate to electrochemically synthesized Cu NWs.

In order to assess the morphologic and geometrical features of Cu NWs against the time duration of the cathodic process, chronoamperometric curves were recorded in the two aqueous electrolytes involved, as illustrated in Fig. 3.
The shapes of the recorded chronoamperograms are quite similar to those reported in literature [6,16]. Several characteristic regions may be noticed, respectively:

(i) a sharp increase of the current at the beginning of the process, usually assigned to the charging of the double layer and the creation of the diffusion layer;
(ii) nanowire growth inside the channels with nearly constant current;
(iii) more or less sharp current increase when the grown material reaches the top side of the membrane and caps start to grow on top, and

(iv) if the process continues, the caps grow further and eventually form a continuous layer at an almost constant current.

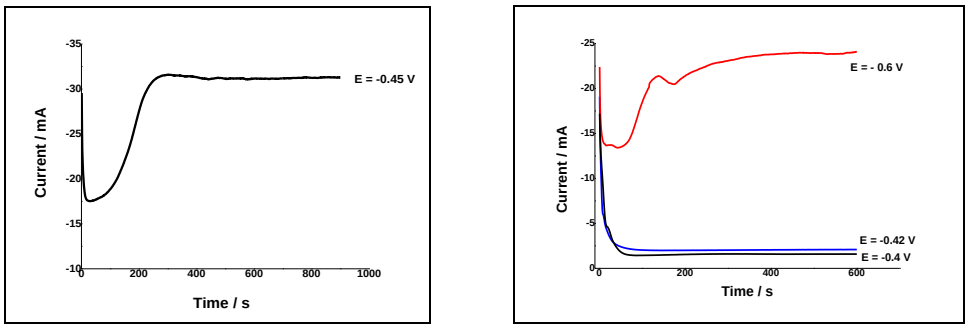


Fig. 3. Chronoamperometric curves recorded during electrochemical preparation of Cu NWs on PC membrane template at 25 °C using: (a) 0.8 M $CuSO_4$ + 0.6 M H_2SO_4 electrolyte at a cathodic potential of -0.45 V vs. Ag/AgCl and (b) 0.8 M $CuSO_4$ + 0.6 M H_2SO_4 + 4 mL/L wetting agent at various cathodic potentials

Fig. 4 presents SEM micrographs of Cu NWs potentiostatically deposited at -0.45 V *vs.* Ag/AgCl for 15 min, involving a PC membrane with 400 nm pore diameter. The top view image in Fig. 4a clearly evidences the presence of Cu layer covering entirely the membrane surface. The cross-section views (Figs 4b-d) confirm the Cu NWs formation, relatively firmly anchored in the metallic conducting substrate on the PC membrane.

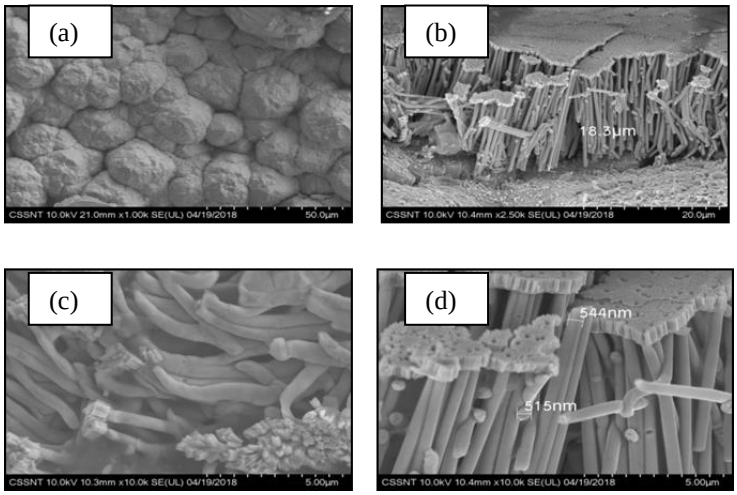


Fig. 4. SEM micrographs of Cu nanowires potentiostatically grown from 0.8 M $CuSO_4$ + 0.6 M H_2SO_4 electrolyte at -0.45 V vs. Ag/AgCl for 15 min using PC membrane template with 400 nm pore diameter: (a) top view and (b-d) cross-section views

It is worth to notice the diameter of the synthesized Cu NWs, of 515-545 nm, which is quite larger as compared to the membrane pore nominal diameter of 400 nm. Similar results have been reported in [16]. Two possible reasons are considered for a higher diameter of NWs: on one hand, a non-uniformity of the pores diameter inside the membrane may be taken into account; on the other hand, an enlargement of the pores during the electrochemical growth process could occur if the metal deposition takes place not only along the direction of pore axis but to a certain degree radially as well, thus exerting pressure onto the PC membrane which causes a widening of the pores [16].

Fig. 5 shows examples of SEM micrographs of Cu NWs grown in the optimum cathodic potential, of -0.4 ÷ -0.42 V vs. Ag/AgCl, using as electrolyte 0.8 M $CuSO_4$ + 0.6 M H_2SO_4 + 4 mL.L^{-1} wetting agent. The surface morphology clearly evidences the presence of Cu NWs quite uniformly distributed.

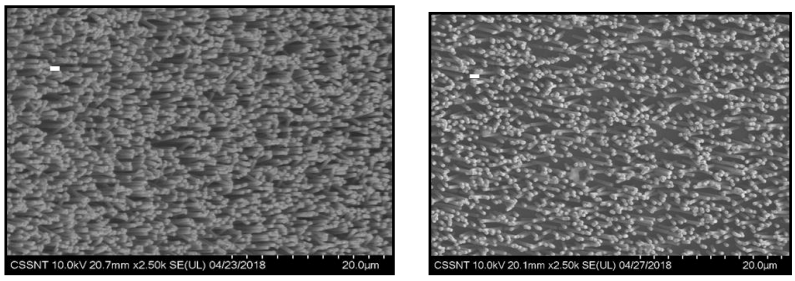


Fig. 5. SEM images of the nanostructured electrode having Cu nanowires grown at different potentials in the optimum cathodic range (25 °C, 0.8 M $CuSO_4$ + 0.6 M H_2SO_4 + 4 mL.L^{-1} wetting agent solution)

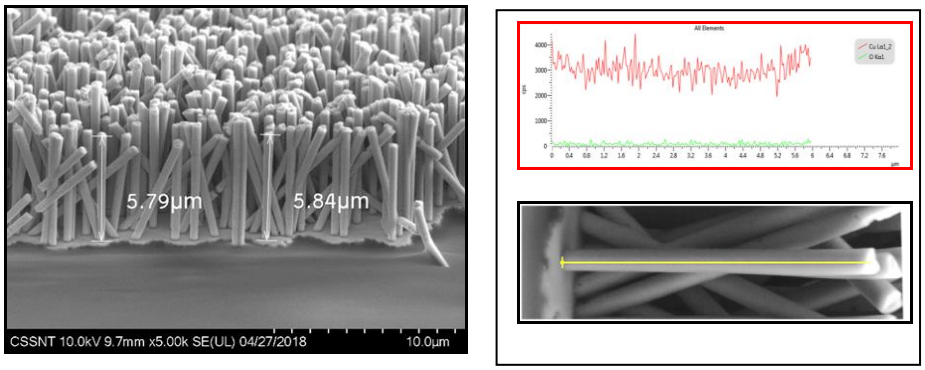


Fig. 6. SEM cross-section views of the nanostructured electrode having Cu nanowires grown at -0.4 V vs. Ag/AgCl for 10 min and EDX elements distribution along the wire (0.8 M $CuSO_4$ + 0.6 M H_2SO_4 + 4 mL.L^{-1} wetting agent)

Usually, the electrochemically synthesized Cu NWs under potentiostatic conditions presented an adequate longitudinal homogeneity from composition view point, as shown in Fig. 6. In addition, the EDX elemental analysis evidenced the presence of about 2-6 at. % O besides Cu, an expected experimental result taking into account that Cu is an easily oxidizable metal under atmospheric conditions.

To get more information on the crystallinity of the synthesized Cu NWs the X-ray diffraction analysis was performed on nanowires still embedded in PC membrane. Fig. 7 shows a typical X-ray pattern, evidencing the presence of metallic Cu characteristic peaks.

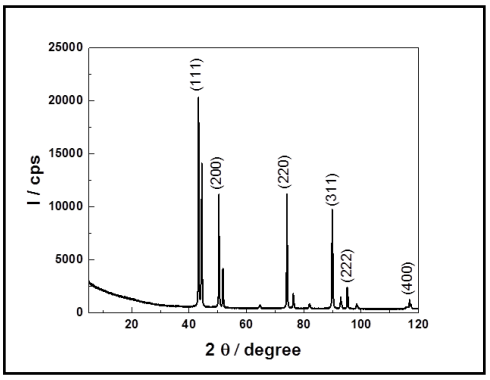


Fig. 7. XRD pattern of Cu nanowires electrochemically grown at -0.4 V vs. Ag/AgCl for 10 min (0.8 M $CuSO_4$ + 0.6 M H_2SO_4 + 4 $mL.L^{-1}$ wetting agent)

The Cu nanowires presented patterns with three intense peaks, with the highest for the (111) crystal plane and the other two lower peaks at (200) and (220), regardless the value of the applied cathodic potential. All the intense XRD peaks were at the same positions as for the polycrystalline copper standard (PDF card No. 00-004-0836), indicating that copper nanowires with face-centred cubic crystal structures had been synthesized.

3.2 Electrochemical synthesis of Cu NWs involving deep eutectic solvents (DES)

Deep eutectic solvents, firstly developed by Abbott and coworkers [28,29], consisting in eutectic mixtures of quaternary ammonium salts with either a hydrogen bond donor such as urea, ethylene glycol, glycerol, organic acids or metal salts, have continuously attracted significant attention as "green electrolytes" for a large range of metals and alloys electrodeposition [30-32 and included references]. They represent low cost alternatives to traditional room temperature ionic liquids having low vapor pressure, wide liquid-phase range and

greater electrochemical and thermal stability [30]. In addition, DES have been successfully applied as electrolytes for electrochemical synthesis of various nanostructured materials, including nanoparticles, oxide nanopowders and nanowires [33-35]. However, only few studies on electrodeposition of metallic nanowires in ionic liquids based on choline chloride have been carried out so far [35,36].

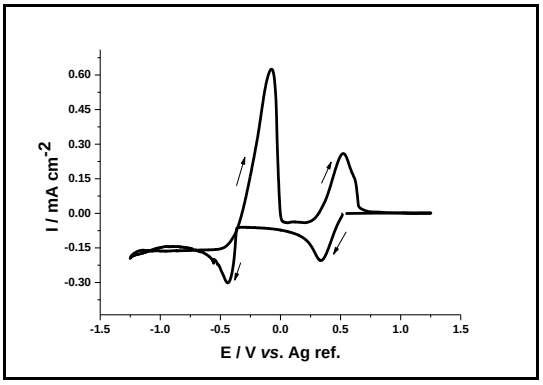


Fig. 8. Cyclic voltammogram of Cu^{2+}/Cu^{o} process from 0.4 M $CuCl_2$ in ILEG at 65 °C on Au sputtered PC membrane as WE. The scan was started at +0.52 V) and the scan rate was 10 mV s^{-1}

A DES electrolyte based on the eutectic mixture of choline chloride with ethylene glycol (denoted ILEG) containing 0.4 M $CuCl_2$ (see Table 1) was tested to prepare Cu NWs into the pores of a PC membrane. Fig. 8 presents the recorded cyclic voltammogram for the Au sputtered PC membrane as the working electrode involving 0.4 M $CuCl_2$ in ILEG as electrolyte, at 65 °C.

As shown in Fig. 8, the reduction of Cu^{2+} to metallic Cu occurs in two steps: first Cu^{+} is formed at a potential of ≈ +0.366 V and in the second step the metal is deposited. The Cu^{2+}/Cu^{+} couple is a reversible redox homogeneous process controlled by diffusion. For the second Cu^{+}/Cu^{o} couple, the potential for cathodic peak is evidenced at about -0.417 V. The shape of the recorded CV suggests a quasi-reversible process, with a high non-compensated ohmic drop in the electrolyte which explains the large cathodic/anodic peak separation (400-700 mV). This behavior has been also reported in [37] and is usually noticed in the case of high ohmic resistance of electrolyte, which is often a characteristic of ionic liquid-based electrolytes. This result can explain the slow kinetics of the reaction, too.

According to Fig. 8, the formation potential of the metallic Cu is around -0.4 V. Therefore, the cathodic potential for the electrochemical preparation of Cu NWs has been selected in the range of -0.4 ÷ -0.45 V. Fig. 9 shows examples of the recorded chronoamperometric curves.

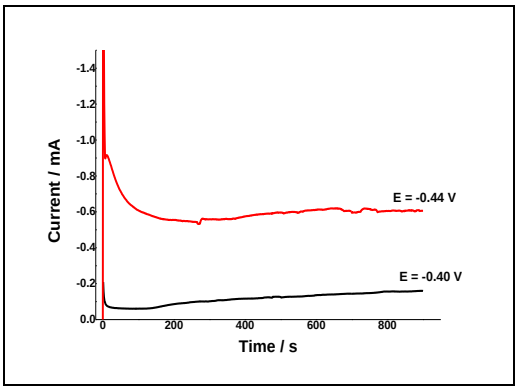


Fig. 9. Chronoamperometric curves recorded during electrochemical preparation of Cu nanowires in PC membrane template (80 nm pore diameter) in ILEG-0.4M $CuCl_2$ at 65ºC at various cathodic potentials, for 15 min

The shape of the recorded chronoamperograms is quite comparable to those obtained in the case of aqueous electrolytes. However, lower current values are evidenced, due to the higher viscosity and lower diffusion coefficients of copper ions in the DES based electrolyte as compared to aqueous ones.

Fig. 10 presents SEM micrographs of the electrochemically prepared Cu NWs involving ILEG based electrolyte. A PC membrane having the nominal pore diameter of 80 nm has been used as template.

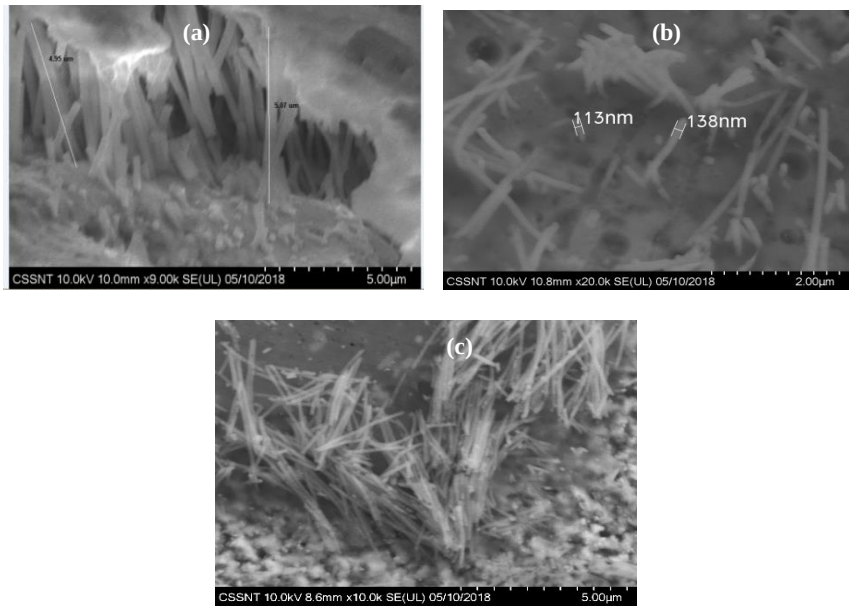
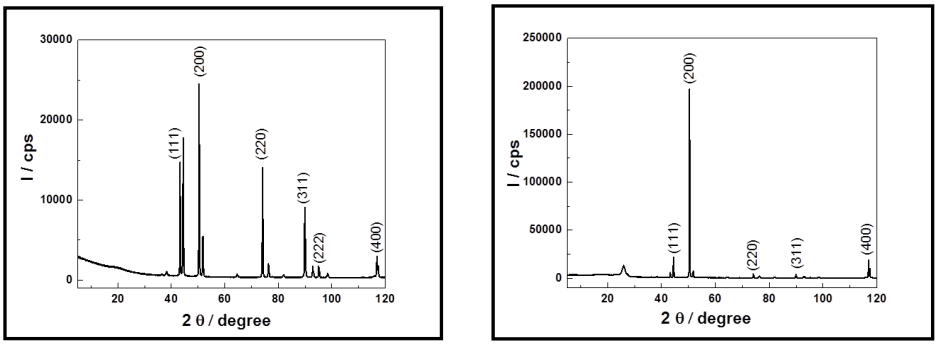


Fig. 10. SEM images of the Cu nanowires electrochemically grown at -0.4 V (a, b) and -0.44 V (c) in ILEG-0.4 M $CuCl_2$ (65 ºC, 15 min) in PC membrane template (80 nm pore diameter)

As shown in Fig. 10, the synthesized Cu NWs seem to be more fragile, being more susceptible to cracking under manipulation during PC membrane dissolution. This behavior might be related either to the smaller diameter of the wires or to the nature of the involved electrolyte. The DES based solution is more viscous as compared to aqueous electrolytes and may affect the entering of the electroactive species into the membrane pores. Again, the diameter of the synthesized Cu NWs, of 110-140 nm, was relatively larger than the membrane pore nominal diameter of 80 nm which may be due to the non-uniformity of the pores diameter or to the metal deposition that could occur not only along the direction of pore axis but radially as well, thus applying pressure onto the PC membrane and causing a widening of the pores [16].

Nevertheless, the obtained results showed that nanowires synthesis is possible from choline chloride based ionic liquids. A higher working temperature is recommended in order to facilitate a better penetration of the electrolyte inside the pores of membrane and consequently to grow more robust nanowires.

To assess the influence of the involved DES based electrolyte on the crystallinity of the synthesized Cu NWs, X-ray diffraction analysis was performed on nanowires still embedded in PC membrane. Fig. 11 shows typical X-ray patterns.



(a) (b)

Fig. 11. XRD patterns of Cu nanowires electrochemically grown at -0.4 V *vs.* Ag ref. (a) and -0.44 V *vs.* Ag ref. (b) for 15 min (0.4 M $CuCl_2$ in ILEG, 65 ^oC)

The XRD analysis revealed the presence of metallic Cu characteristic peaks. The Cu nanowires fabricated at different applied potentials show three intense peaks, with the highest for the (200) crystal plane and the other two lower peaks at (111) and (220). It is worth to mention in this point that the obtained XRD results suggest that the use of DES based electrolytes during electrochemical preparation of Cu NWs may influence their preferred crystallographic orientation.

3.3. Electrochemical sensing performance of Cu NWs for non-enzymatic glucose detection

The performance of Cu NWs has been investigated by analyzing the electrochemical sensing results of the cyclic voltammograms and amperometric current responses in 50 mM NaOH solution with and without glucose addition at a scan rate of 20 mV s^{-1}, as presented in Fig. 12.

The shape of the CV in the absence of glucose and in alkaline environment is quite similar to those reported in [27]. Thus, during anodic scan, oxidation peaks at about -0.574 V and -0.315 V (*vs.* Ag/AgCl) are evidenced, usually assigned to the transition of Cu(0) to Cu(I) and the further oxidation of Cu(0)/Cu(I) to Cu(II). A weak shoulder at around +0.05 V is also present, attributed to the formation of Cu (III) soluble species such as $HCuO_2^-$; this species can occur as a result of Cu-based solids reacting with hydroxide ions [27,38]. In the reverse scan, the peaks at around +0.42 V, -0.81 V and -1.036 V correspond to the symmetric cathodic transitions of Cu(III) to Cu(II), Cu(II) to Cu(I)/Cu(0) and Cu(I) to Cu(0), respectively [27,38].

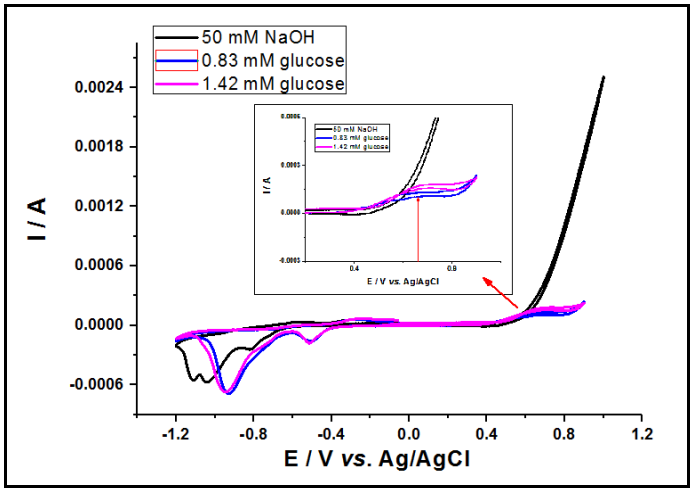


Fig. 12. Cyclic voltammograms of the Cu NWs working electrode in the absence and in the presence of various glucose concentrations. The electrolyte was 50 mM NaOH aqueous solution and the scan rate was 20 mV s^{-1}.

When the glucose is added to the system, the positions of the reduction and oxidation peaks are shifted to slightly more electropositive potentials. In addition, a new shoulder peak is noticed which is attributed to the glucose oxidation at around +0.71 V (*vs.* Ag/AgCl), whose intensity is proportional to the glucose concentration. Moreover, the peak related to the transition of Cu(III/

Cu(II) in the cathodic scan is absent, suggesting that the Cu(III) species are consumed in the electrooxidation of glucose [27,38,39].

On the basis of the CV analysis related to Fig. 12, further steady state amperometric measurements have been carried out (Fig. 13).

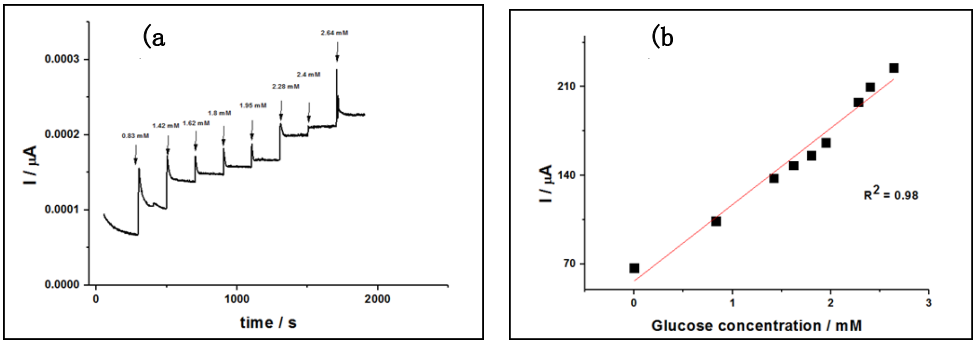


Fig. 13. (a) Amperometric response of the Cu NWs as WE in 50 mM NaOH aqueous solution to the successive addition of glucose at E =+0.71 V/ Ag/AgCl; (b) Corresponding calibration curve

The biased potential was +0.71 V, corresponding to the characteristic anodic peak attributable to glucose oxidation according to Fig. 12.

Fig. 13a shows the current-time (i-t) curves of Cu NWs based electrode by successive injections of glucose solution into the 50 mM NaOH solution at +0.71 V (*vs*. Ag/AgCl) and the corresponding calibration plot (Fig. 13b). During successive injection of glucose, the Cu NWs based electrode presented large step-like increase of the current, which reaches quite instantly the steady-state equilibrium, indicating an attractive short response time. In addition, a reasonable value of 0.98 for correlation coefficient R^2 has been determined, suggesting that the synthesized Cu NWs might represent a potential candidate as glucose sensor material.

4. Conclusions

The Cu nanowires have been successfully synthesized using template-assisted method from aqueous electrolytes and choline chloride based ionic liquids. SEM images showed that relatively homogeneously distributed ensembles of Cu nanowires have been obtained, with lengths in the range 3-18 μm, depending on the involved electrolyte and applied cathodic potential.

The XRD analysis revealed the presence of metallic Cu characteristic peaks. The nature of the electrolyte (aqueous / DES) may influence their preferred crystallographic orientation. When aqueous electrolyte was used, the highest XRD peak was noticed for the (111) crystal plane, while in the case of DES based

electrolyte one the the highest XRD peak for (200) crystal plane orientation was observed.

Preliminary results suggested that the synthesized Cu nanowire electrodes may act as electrochemical sensing element for enzyme-free amperometric detection of glucose.

Future detailed investigations are scheduled for the optimization of Cu nanowire electrodes fabrication with an adequate reproducibility, durability and stability against glucose detection.

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