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Electrodeposition of nanocrystalline silver films and nanowires from the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate

Sherif Zein El Abedin[a,b], F. Endres[a,*]

[a] Institute of Particle Technology, Clausthal University of Technology, Robert-Koch-Strasse 42, D-38678 Clausthal-Zellerfeld, Germany
[b] Electrochemistry and Corrosion Laboratory, National Research Centre, Dokki, Cairo, Egypt

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ABSTRACT

We report in this paper on the electrodeposition of nanocrystalline silver films and nanowires in the air and water stable ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate [EMIm]TfO containing Ag(TfO) as a source of silver. The study was performed by means of cyclic voltammetry and chronoamperometry, and the electrodeposits were characterized by SEM-EDX and XRD. The cyclic voltammetry behaviour showed typical reduction and oxidation peaks corresponding to the deposition and stripping of silver in the employed electrolyte. XRD patterns of the electrodeposited silver layers revealed the characteristic peaks of crystalline silver with crystallites in the nanosize regime. Silver nanowires with average diameters and lengths of about 200 nm and 3 μm, respectively, were prepared by potentiostatic deposition within a commercial nuclear track-etched polycarbonate template.

1. Introduction

Nowadays, electrodeposition from ionic liquids has received extensive attention due to their unique properties. The recent efforts on the electrodeposition from ionic liquids, challenges and prospects have been described and discussed in [1]. In principle, most of the metals and alloys that can be electrodeposited from aqueous solutions can also be electrodeposited from ionic liquids. Since many of the ionic liquids are environmentally friendly, they are considered as suitable alternatives for many poisonous electroplating baths. Furthermore, as ionic liquids have very low vapour pressures (often between 10^{-11} and 10^{-10} mbar at or near room temperature, at 100 °C the vapour pressure is – depending on the liquid – in the region of 10^{-6} to 10^{-4} mbar), thus, they can be used in open galvanic baths at variable temperatures without releasing of harmful vapours which reduces the amount of volatile organic compounds released into the atmosphere. Another advantage of using ionic liquids instead of aqueous baths is that the thermal stability of ionic liquids makes it easier to electrodeposit crystalline metals and semiconductors through direct electrodeposition at elevated temperatures, above 100 °C, without subsequent annealing. Moreover, there is no hydrogen embrittlement due to the hydrophobic nature of many ionic liquids, that only slowly absorb water under air.

Despite the unique properties of ionic liquids as solvents for electrodeposition some challenges have to be considered such as, impurities, cation/anion effects or viscositiy/conductivity. Using pure ionic liquids in the electrodeposition is recommended as the impurities would influence the quality of the deposit. Furthermore awareness of the cation/anion effects is necessary in order to avoid unexpected influence resulting from employing of unsuitable cation/anion. Compared with aqueous electrolytes the viscosity of ionic liquids is high and the specific conductivity is low which lead to low deposition rate. This could be improved just by heating as at about 100 °C the viscosity of many ionic liquids approaches that of water.

In general, ionic liquids can be regarded as a potential replacement for many aqueous electroplating baths, especially the toxic ones like cyanide baths for silver electroplating. The electrodeposition of silver from chloroaluminate ionic liquids is straightforward [2]. However, these ionic liquids are extremely hygroscopic and they must be prepared and handled under inert gas atmosphere. Katayama et al. [3] reported that the – more or less – water insensitive ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm]BF_4) is applicable as an alternative electroplating bath for silver. Electrodeposition of silver in the ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF_4) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF_6) was reported [4]. Bardi and coworkers [5] showed the capability of depositing very thin (~0.3 μm), adherent silver layers on commercial grade copper substrates in the ionic liquid [BMIm]BF_4 at variable temperatures, up to 200 °C. Furthermore, templated

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* Corresponding author. Tel.: +49 5323 72 3141; fax: +49 5323 722460.
E-mail address: frank.endres@tu-clausthal.de (F. Endres).

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electrodeposition of silver nanowires in $[BMIm]PF_6$ was reported [6]. Although these ionic liquids are often regarded as water insensitive, the exposure to moisture for a long time sometimes causes some changes in their physical and chemical properties. This leads to a partial decomposition of the ionic liquids generating HF which is pretty aggressive. Thus, ionic liquids based on more stable anions such as trifluoromethylsulfonate ($CF_3SO_3^-$), bis(trifluoromethylsulfonyl) amide [$(CF_3SO_2)_2N^-$] and tris(trifluoromethylsulfonyl) methide [$(CF_3SO_2)_3C^-$] might be quite promising as new electroplating baths. Recently, we showed for the first time that isolated, dispersed silver nanoparticles with an average diameter of 20 nm can be deposited on the surface of the ionic liquid 1-butyl-3-methylimidazolium trifluoromethylsulfonate ([BMIm]TfO) by electrochemical reduction with free electrons from a low temperature plasma [7,8].

In the present paper we report on the electrodeposition of nanocrystalline films and nanowires of silver in the air and water stable ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate ([EMIm]TfO) using Ag(TfO) as a source of silver. Silver nanowires were prepared by potentiostatic deposition within a commercial nuclear track-etched polycarbonate template.

2. Experimental

The electrodeposition of silver was studied in the water and air stable ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate [EMIm]TfO with high purity (Merck). The ionic liquid was used as received without further purification or drying. The viscosity and conductivity of the employed ionic liquid at 20 °C were reported to be 45 mPa s and 8.6 mS cm^{-1}, respectively [9]. Silver trifluoromethylsulfonate (Alfa, 99%) was used as a source of silver due to its high solubility in the employed ionic liquid.

All electrochemical measurements were performed using a Verstat 263A Potentiostat/Galvanostat (Princeton Applied Research) controlled by PowerCV and PowerStep software. The experiments were carried out under air with a relative humidity of about 50% at 20 °C. In cyclic voltammograms measured on gold there is no evidence for electrochemically active water on a timescale of about 1 h under air. Gold substrates from Arrandee (gold films of 200–300 nm thickness deposited on chromium-covered borosilicate glass) and glassy carbon substrates (Alfa) were used as working electrodes, respectively. Directly before use, the gold substrates were very carefully heated in a hydrogen flame to red glow. Glassy carbon substrates were cleaned for 10 min in an ultrasonic bath in acetone followed by refluxing in isopropanol. For Ag-nanowires synthesis, nuclear track-etched polycarbonate membranes (Millipore) with pore diameters of 100 nm were used as templates. The back side of the membrane was sputtered by a roughly 100 nm thick gold film to serve as a working electrode. The Au-coated side was placed onto a copper plate connected to the potentiostat. The electrochemical cell made of polytetrafluoroethylene (Teflon) was clamped over a Teflon covered Viton o-ring onto the other side of the membrane, thus yielding an exposed surface area of 0.6 cm^2. A platinum wire (Alfa, 99.99%) and a silver wire (Alfa, 99.99%) were used as counter and reference electrodes, respectively. The electrode potential of the reference electrode was calibrated in several experiments vs. ferrocene/ferrocinium. Its electrode potential exhibits sufficient stability throughout the experiments. The redox couple ferrocene/ferrocinium has a value of +320 mV vs. Ag reference.

A high resolution field emission scanning electron microscope (Carl Zeiss DSM 982 Gemini) was utilized to investigate the surface morphology of the deposited films and energy dispersive X-ray analysis was used to determine the film composition. The X-ray diffractograms of the deposited silver samples were recorded using a Siemens D-5000 diffractometer with Co Kα radiation.

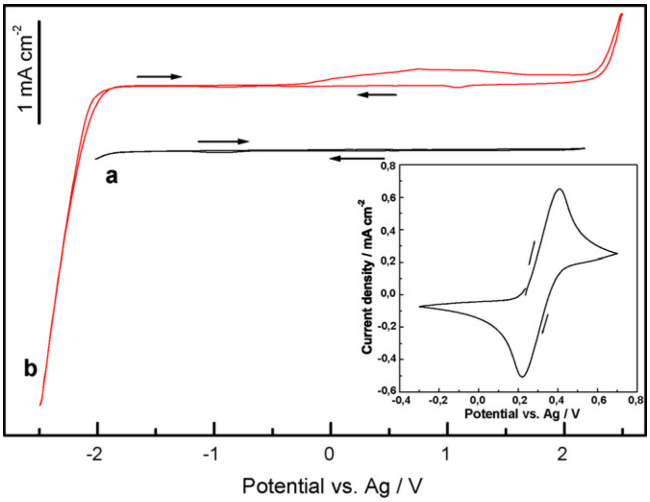

Fig. 1. Cyclic voltammograms of the ionic liquid [EMIm]TfO on gold with different reversal potentials. Inset: cyclic voltammogram of the ionic liquid [EMIm]TfO containing 50 mmol/l ferrocene on gold. The scan rate was 10 mV s^{-1}.

3. Results and discussion

3.1. Electrodeposition of silver films

3.1.1. Cyclic voltammetry

Fig. 1 shows the electrochemical window of the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate [EMIm]TfO on gold under air. As seen, the employed ionic liquid exhibits an electrochemical window of about 4.3 V, extending from −2.0 to +2.3 V vs. Ag quasi-reference. The cathodic and anodic limiting potentials were evaluated when the reduction and oxidation currents reached 100 μA cm^{-2}. This current value is called cut-off current density. Usually the cut-off current density is selected between 0.1 and 1.0 mA cm^{-2} [10]. However, it is more common to select the cut-off current density below 0.1 mA cm^{-2}. The cathodic and anodic limits of the cyclic voltammogram are corresponding to the reduction of $[EMIm]^+$ cation and the oxidation of gold and/or anodic decomposition of TFO^- anion, respectively (Fig. 1, curve b). The increase in anodic current starting at a potential of about −0.1 V is attributable to the oxidation of the reduction products of $[EMIm]^+$ formed on the preceding cathodic scan. If the potential is reversed before the cathodic decomposition of $[EMIm]^+$ sets in, no pronounced anodic current was recorded up to a potential of +2.2 vs. Ag confirming the former interpretation (Fig. 1, curve a). As all potentials in this study were measured vs. Ag reference electrode the potential of the redox couple feerocene/ferrocinium was measured in the employed ionic liquid to give a known reference electrode potential, see inset of Fig. 1. The redox couple ferrocene/ferrocinium has a value of +320 mV vs. Ag.

The cyclic voltammetry behaviour of the ionic liquid [EMIm]TFO containing 0.2 M Ag(TfO) on gold is displayed in Fig. 2a. It is clearly seen that the cyclic voltammogram exhibits a clear redox couple. The observed reduction peak is due to the bulk deposition of Ag and the anodic peak is due to stripping of the deposited silver. The ratio of the anodic to cathodic charges (Q_a/Q_c) determined from the integrated peak areas in the voltammogram was close to unity. Beyond the recorded anodic peak, the current reaches zero indicating the complete stripping of the deposited silver obtained in the forward scan.

The cyclic voltammetry behaviour of the employed ionic liquid containing 0.2 mol/l Ag(TfO) was also recorded on glassy carbon (Fig. 2b). As seen, the cyclic voltammogram shows the reduction and oxidation peaks corresponding to the deposition and stripping

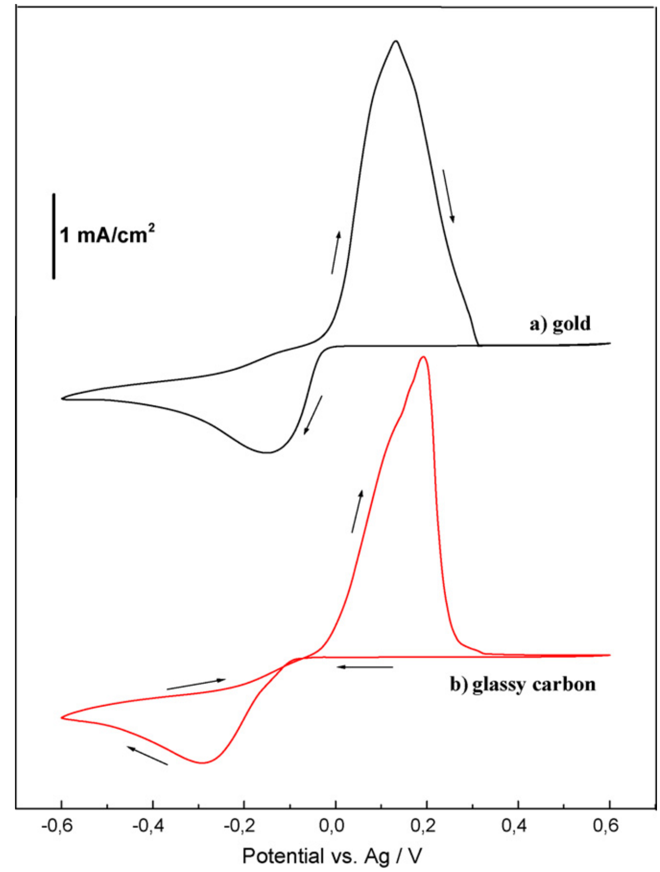

Fig. 2. Cyclic voltammograms of the ionic liquid [EMIm]TfO containing 0.2 mol/l Ag(TfO) recorded on (a) gold and (b) glassy carbon at a scan rate of 10 mV s^{-1}.

of silver. The ratio of the anodic to cathodic charges of the anodic and cathodic peaks, respectively, was close to unity, indicating the complete stripping of the electrodeposited silver. In the reverse scan, a crossover loop was observed, indicating a nucleation process. This means that the electrodeposition of Ag on glassy carbon requires an overpotential to initiate nucleation and growth of Ag bulk deposition.

3.1.2. Characterization of electrodeposited Ag films

Potentiostatic electrodeposition of silver was performed on gold and on glassy carbon substrates at a potential of −0.3 V for 2 h in [EMIm]TfO containing 0.2 mol/l Ag(TfO). The electrodeposited silver layers were characterized by SEM-EDX and XRD to explore surface morphology, composition and crystal structure, respectively. Visually, a white silver deposit was obtained after potentiostatic electrodeposition experiments. Following the deposition experiments the deposits were washed thoroughly with isopropanol and then cleaned with acetone in an ultrasonic bath for about 3 min. This cleaning process is to remove the residual ionic liquids. EDX analysis of the electrodeposited layers reveals that only pure silver was deposited on the electrode surface. There was no trace of any component of the ionic liquid in the deposits, indicating the complete removal of the residual ionic liquid during the rinsing process.

The SEM micrograph of Fig. 3a presents the surface morphology of a deposited silver layer obtained on gold. The Ag deposit appears to be nodular containing large agglomerated crystallites in the order of 0.5–1 μm in size. Each of the silver crystallites consists of small grains of sizes in the nanometer regime, as revealed in the inset of Fig. 3a which shows a higher magnification SEM micrograph. The EDX analysis shows only silver (Fig. 3b). The morphology of the deposited silver layer obtained on glassy carbon is shown in Fig. 4a. Similar to the deposit obtained on gold, the deposited silver layer contains large crystallites formed by agglomeration of fine crystallites. Furthermore, the deposit contains very fine crystallites in the nanometer regime, see the inset of Fig. 4a. It is also seen that the deposit is porous giving rise to high surface area which might lead to increased catalytic activity of the deposited silver owing to its high surface to volume ratio. The electrodeposit was analysed as pure silver as revealed in the accompanied EDX profile of Fig. 4b. In the light of the SEM results, it can be concluded that the electrodeposition of Ag involves first the formation of fine crystallites in the nanometer regime followed by crystallites agglomeration.

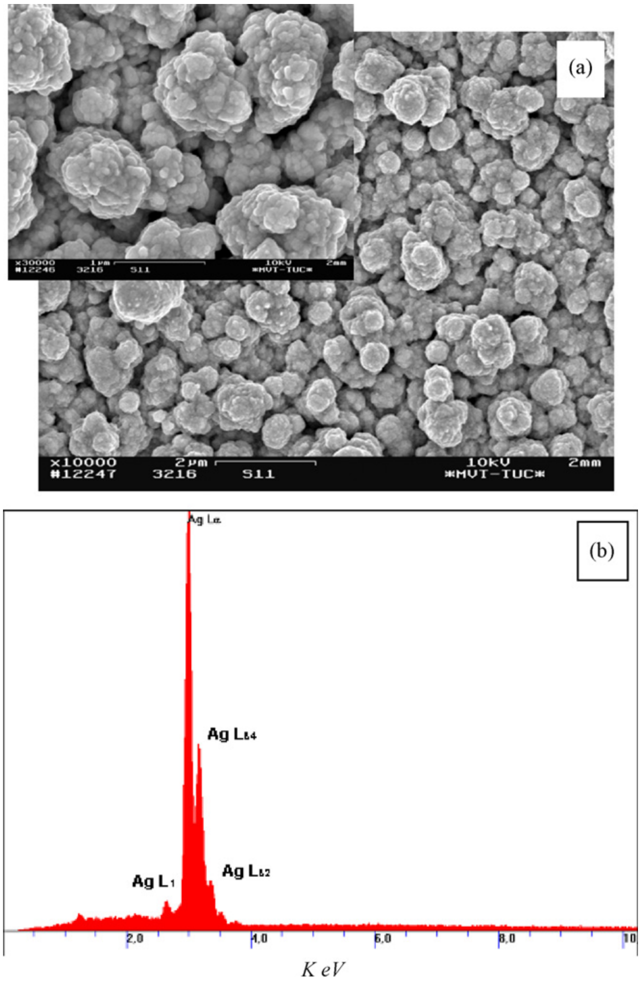

Fig. 3. (a) SEM micrograph of an about 4 μm Ag-layer electrodeposited on gold in the ionic liquid [EMIm]TfO containing 0.2 mol/l Ag(TfO) at a potential of −0.3 V vs. Ag for 2 h. Inset: SEM micrograph of higher magnification. (b) EDX analysis of the area shown in the SEM micrograph of lower magnification.

The XRD patterns shown in Fig. 5 exhibit five pronounced diffraction peaks at $2\theta = 44.56°$, 51.90°, 76.48°, 93.21° and 98.62° which agree well with the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) diffractions of face centred cubic silver (JCPDS File No. 04-0783). This confirms the metallic state of the coated silver. As seen in Fig. 5, the recorded peaks are broad indicating the small crystallite size of the electrodeposited silver film. The average crystallite size of Ag was estimated according to Scherrer's equation [11]:

$$d = 0.9\lambda/\beta_{1/2}\cos\theta \qquad (1)$$

where d is the crystallite size, λ the x-ray wavelength (1.7889 Å for Co Kα), $\beta_{1/2}$ the full-width half maximum (FWHM) and θ is the diffraction angle. The inset of Fig. 5 shows the estimation of the

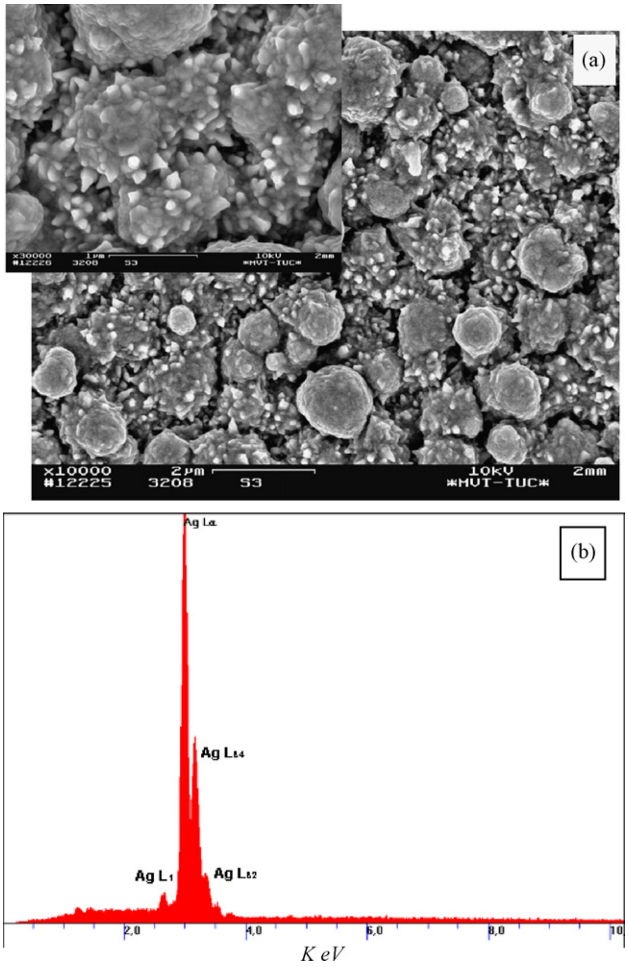

Fig. 4. (a) SEM micrograph of an about 4 μm Ag-layer electrodeposited on glassy carbon in the ionic liquid [EMIm]TfO containing 0.2 mol/l Ag(TfO) at a potential of −0.3 V vs. Ag for 2 h. Inset: SEM micrograph of higher magnification. (b) EDX analysis of the area shown in the SEM micrograph of lower magnification.

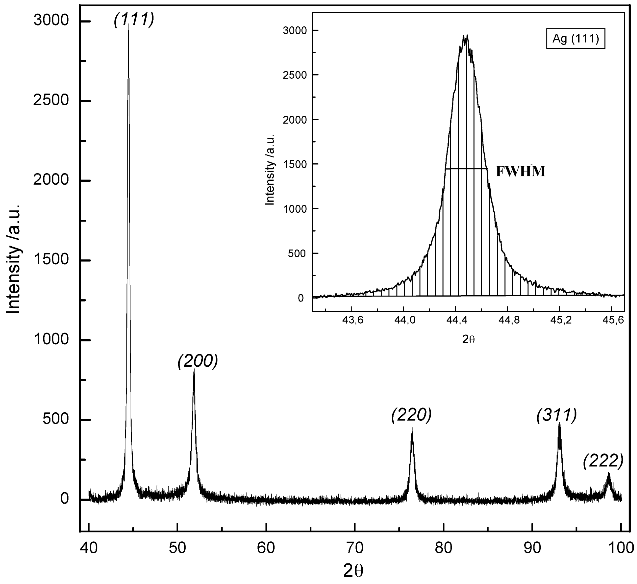

Fig. 5. XRD patterns of an electrodeposited Ag layer obtained on glassy carbon in the ionic liquid [EMIm]TfO containing 0.2 mol/l Ag(TfO) at a potential of −0.3 V vs. Ag for 2 h. Inset: FWHM of Ag(1 1 1) peak of XRD patterns.

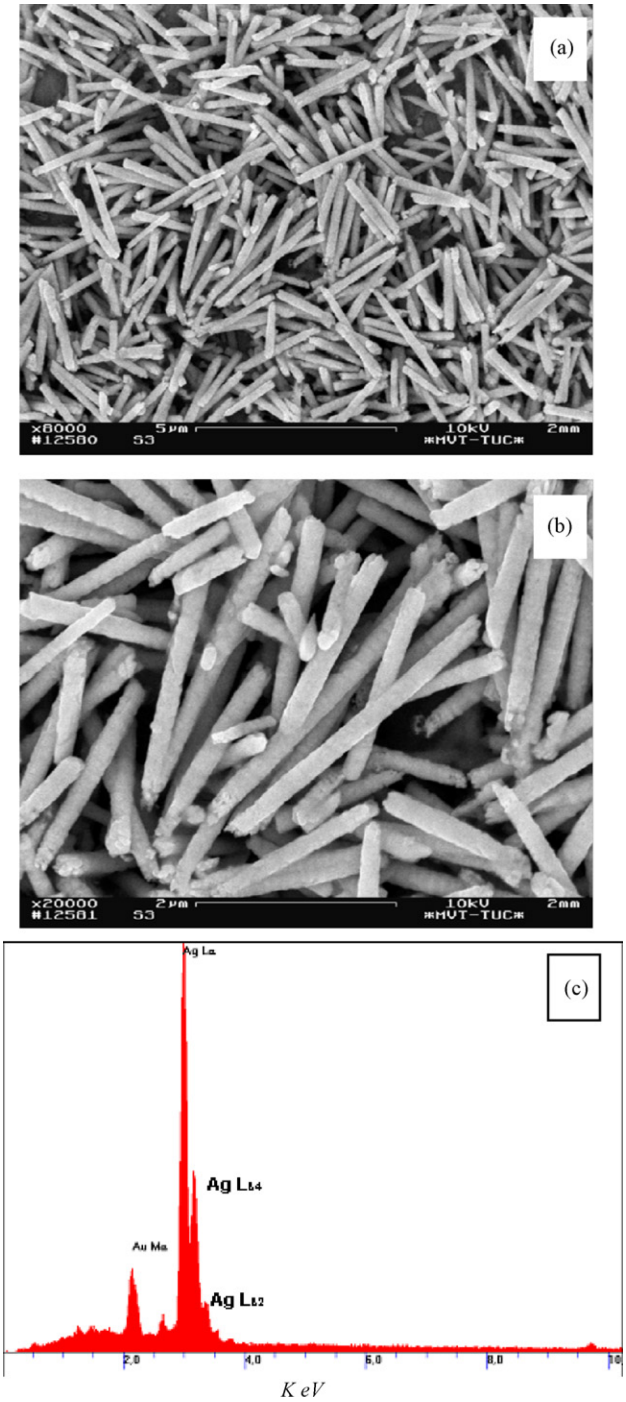

Fig. 6. (a) SEM micrograph of Ag nanowires obtained in the ionic liquid [EMIm]TfO containing 0.2 mol/l Ag(TfO) at a potential of −0.3 V vs. Ag for 4 h. (b) SEM micrograph of higher magnification. (c) EDX analysis of the area shown in the SEM micrograph of lower magnification.

full-width half maximum of the Ag(1 1 1) peak, as an example, of XRD patterns of the electrodeposited Ag layer. The average size of Ag crystallites was found to be 35 nm.

3.2. Electrodeposition of silver nanowires

Due to their potential applications in many areas, e.g. electronics, sensors and catalysis, nanowires, especially metal nanowires, have attracted extensive attention. Silver nanowires are of particular interest due to their excellent electrical and thermal conductivities and high stability [12]. Furthermore, the high surface area of silver nanowires gives rise to increased catalytic activity when they are employed as a catalyst.

Template-assisted electrodeposition is an elegant and economic approach for the synthesis of metal nanowires and it is currently widely used. The use of templates permits the synthesis of well-defined nanowires with controllable size and shape. Commercially available anodic aluminium oxide (AAO) and nuclear track-etched polycarbonate (PC) membranes are commonly used as nanoporous templates. Electrodeposition of silver nanowires using (AAO) templates in aqueous solutions was reported [13–15]. Quite recently synthesis of silver nanowires using PC templates in the ionic liquid [EMIm]PF_6 was reported [6]. Silver ions were introduced into the solution by anodic dissolution of silver metal in the employed ionic liquid [6]. It should be mentioned that the use of ionic liquids based on anions like PF_6^- or BF_4^- as electrolytes for electrodeposition is no longer recommended by the ionic liquids community. Although these ionic liquids can be regarded as water stable they partially decompose by long exposure to air generating HF which is rather aggressive. Hence they cannot be employed as electrolytes in open baths. Therefore, the ionic liquid [EMIm]TfO was employed in our study as it is well suited for use under air to make the synthesis process more versatile and simple.

Silver nanowires were prepared in a PC membrane at a constant potential of −0.3 V for 4 h in [EMIm]TfO containing 0.2 mol/l Ag(TfO). The electrodeposition of the silver nanowires starts on the gold cathode at the bottom of the pores and grow along the pores. Fig. 6 shows typical SEM micrographs of silver nanowires after removal of the PC membrane by dissolution in dichloromethane. As shown in the SEM micrograph of Fig. 6a the electrodeposited Ag nanowires are highly dense. The average diameters and lengths of the synthesized nanowires are about 200 nm and 3 μm, respectively (Fig. 6b). The measured diameter of the obtained nanowires is significantly larger than the pore diameter quoted by the producer (100 nm). This is not surprising as the employed commercial PC membranes are mainly fabricated for use as filters, and hence the pore diameter is neither optimized nor precisely defined. Similar results were reported by several authors [16,6]. The measured diameters of Ni, Co, Cu and Au nanowires obtained in aqueous solutions using commercial PC membranes with nominal pore diameters between 10 and 200 nm were higher by up to a factor 3 than the quoted pore diameters [16]. Moreover, it was reported [6] that the average diameter of Ag nanowires obtained in the ionic liquid [EMIm]PF_6 was about 80 nm although the nominal pore diameter was 30 nm. The EDX profile of the nanowires shown in the SEM micrograph of Fig. 6b indicates the deposition of pure silver nanowires (Fig. 6c). The sputtered gold film (working electrode) is also detected in the EDX profile.

4. Conclusions

The present paper shows that air and water stable ionic liquids can be regarded as promising baths to replace toxic cyanide baths for silver electroplating. Furthermore, a simple synthesis approach for Ag-nanowires was presented. In general the advantages of the use of ionic liquids in electroplating baths are not only because they offer environmentally benign conditions for electroplating but also to avoid the problems associated with hydrogen ions in conventional aqueous baths. For example, high quality deposits of metals like Au, Pt and Pd and their alloys can be made in ionic liquids without co-evolution of hydrogen which can alter the quality of the deposits obtained in aqueous solutions.

It was found that silver films and nanowires can be electrodeposited in the air and water stable ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate [EMIm]TfO containing Ag(TfO) as a source of silver under air. The cyclic voltammograms measured on gold and glassy carbon substrates exhibit a redox couple associated with deposition/stripping of silver in the employed electrolyte. A crossover loop was observed in the cyclic voltammogram recorded on glassy carbon, indicating a nucleation process. XRD patterns of the electrodeposited silver layers revealed the characteristics peaks of face centred cubic silver with crystallites in the nanosize regime. Silver nanowires with average diameters and lengths of about 200 nm and 3 μm, respectively, were prepared by potentiostatic deposition within a commercial nuclear track-etched polycarbonate template.

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