



# Tuning the morphology of Te one-dimensional nanostructures by template-free electrochemical deposition in an ionic liquid



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## ABSTRACT

Template-free electrodeposition of Te one-dimensional (1D) nanostructures was carried out from an ionic liquid binary mixture: 1-ethyl-1-octyl-piperidinium bis(trifluoromethylsulfonyl)imide:1-ethyl-1-octyl-piperidinium bromide (EOPipTFSI:EOPipBr 95:5 (mol%)). SAED and XRD analyses confirm the formation of Te 1D nanostructures with a hexagonal single crystalline structure following the [001] direction. A systematic study of the influence of synthesis parameters on the deposits morphology has shown that it is possible to control the shape and the dimensions of the deposited nanostructures. Specifically, the applied potential has a strong influence on the morphology of the deposits. Nanowires or hollow nanostructures can be obtained, depending on mass transport conditions, as confirmed by the use of a soluble anode.

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## 1. Introduction

Tellurium (Te) and its binary or ternary compounds are used in many domains such as piezoelectric devices [1], gas sensors [2], photoconductors [3], solar cells [4] and thermoelectric generators and coolers [5]. Thermoelectricity, which consists in a reversible conversion of heat into electricity and conversely, allows the harvesting of wasted heat and therefore is particularly interesting for the improvement of energy systems efficiency [6]. The thermoelectric performances are evaluated by the figure of merit ZT given by the Eq. (1):

$$ZT = \frac{S^2 \sigma}{K_e + K_g} T \quad (1)$$

where S is the Seebeck coefficient,  $\sigma$  is the electrical conductivity,  $K_e$  is the electronic thermal conductivity,  $K_g$  is the phonon thermal conductivity and T is the temperature.

The performances of thermoelectric compounds can be improved by nanostructuring [6–9]. Among nanostructures, one-dimensional nanostructures like nanowires [10–13] and core-shell nanowires [13–17] are particularly promising due to the high phonon interface scattering and the blocking of the phonon conduction along the wire axis which lead to an increase of the

thermoelectric conversion efficiency. Te nanowires can represent a base to create core-shell structures, being the core that could be further capped with a shell to get arrays of Te-based thermoelectric nanostructures like BiTe [17–20], AgTe [20–22] or LaTe [23].

Various approaches have been developed to synthesize Te nanowires, such as physical and chemical vapor deposition [24,25], hydrothermal process [26–28], galvanic displacement reaction [29–31] or electrochemical deposition (ECD) [32–36]. Arrays of Te 1D nanostructures have already been obtained by ECD, mainly by template-assisted electrodeposition, using anodic aluminium oxide (AAO) [33] or polycarbonate etched membrane templates [34]. However, template-assisted methods involve multiple fabrication steps, like the preparation of the template and its removing which is necessary for the further deposition of a thin upper layer leading to core-shell structures. A single step template-free synthesis route would be more convenient and easier to perform. Room-Temperature Ionic Liquids (RTILs) are promising solvents for template-free synthesis as they can act as capping agents leading to the synthesis of nanostructures. As example, Ma et al. synthesized Te nanowires via a chemical route using triethanolamine tetrafluoroborate ionic liquid as an additive in an aqueous solution [37]. Additionally RTILs present specific advantages for ECD purposes such as a wide electrochemical window, a good electrical conductivity and a high thermal stability which gives access to highly crystalline materials. Template-free electrodeposition of 1D nanostructures in RTILs is little present in the literature. Steichen and Dale showed that selenium nanorods can be grown in an imidazolium-based ionic liquid mixture: 1-ethyl-3-methylimidazolium tetrafluoroborate/chloride [C<sub>2</sub>mim]

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[BF<sub>4</sub>]/[C<sub>2</sub>mIm]Cl [38]. Al nanowires were obtained by Su et al. in a Lewis acidic liquid AlCl<sub>3</sub>/trimethylamine hydrochloride [39]. With the use of imidazolium based ionic liquids, several works highlight the synthesis of metals (Zn [35], Sn [35,40], Co [41]) and alloys (NiZn [42], CuZn [43], AuZn [44] or FeCoZn [45]) nanowires. Very few works were published concerning Te nanostructures synthesis in RTILs. Al-Salman and co-workers recently [35] synthesized long Te polycrystalline nanowires of several micrometers with diameters between 25 and 35 nm in the 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ionic liquid containing SiCl<sub>4</sub>. The authors show in this article that the capping agent is not here the ionic liquid but rather SiCl<sub>4</sub> that promotes the growth of Te nanowires. However, the use of SiCl<sub>4</sub> leads to the presence of an amorphous and passive layer on the surface of the nanowires, composed of Si, C and O, which will alter the electrical properties of these materials.

In a previous work [36], we showed that it is possible to obtain free standing single crystalline Te nanowires at moderate temperature (60–100 °C) in a piperidinium-based ionic liquid mixture: EOPipTFSI:EOPipBr (1-ethyl-1-octylpiperidinium cation, bis(trifluoromethylsulfonyl) imide and bromide anions) without the need of any template. However, the obtained length of the nanowires was limited to 1 μm at best, which is not enough for future applications in thermoelectricity. The morphology, size and organization of the structures are very important characteristics that impact physical and chemical properties of nanostructured materials. The modulation of these parameters can be achieved by varying electrodeposition conditions in order to obtain one-dimensional nanowires with a high length to diameter aspect ratio for optimal thermoelectric properties. In our previous work, only the influence of electrolyte temperature was investigated. It appeared that the best crystallinity of the deposits was obtained at 100 °C. Here, we present a systematic study of other growth parameters like the applied fixed potential and the composition of the electrolyte on the deposits morphology. The morphology of Te electrodeposits was systematically investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). This work shows that 1D nanostructures with different morphologies can be obtained resulting from specific mass transport phenomena.

## 2. Experimental

TeCl<sub>4</sub> (99%, Alfa Aesar) was used as Te precursor. EOPipTFSI and EOPipBr were synthesized according to [46,47] and were characterized by nuclear magnetic resonance analysis (Bruker Spectrospin 300 MHz) and stored in an argon filled glove box (MBraunLabstar; O<sub>2</sub>/H<sub>2</sub>O levels <1 ppm). A mixture of EOPipTFSI and EOPipBr was used as electrolyte. EOPipBr improves the solubility of Te<sup>IV</sup> salts in TFSI-based ionic liquids probably by the formation of complex halide species [48]. As the viscosity strongly increases with the EOPipBr content [49], the amount of EOPipBr was limited to 5% (mol/mol) that represents the best compromise between a good solubility of the Te<sup>IV</sup> salt and a low electrolyte viscosity.

Electrochemical experiments were performed in a glove box using a Biologic potentiostat (VSP300). Platinum-coated glass slides (25 × 10 × 1 mm, Pt coating thickness 300 nm with a thin Cr sublayer that ensures a good adherence of the Pt layer), supplied by Applications Couches Minces (ACM), were used both as working and counter electrodes and a Pt wire was used as quasi-reference electrode. The volume of the bath was equal to 5 mL leading to an immersed slide surface of 0.5 cm<sup>2</sup>. Some specific electroplating synthesis were performed by using a bulk Te anode, which was beforehand prepared by melting Te shots in a square tin at 300 °C.

The resulting metallic block was then polished with successively finer grades of SiC Emery paper up to 2400 before use.

The morphology of the deposits was analyzed by SEM (Philips XL30) at 5 kV. TEM images of individual nanostructures were recorded by a Philips CM200 transmission electron microscope operating at an accelerating voltage of 200 kV. A statistic study from TEM images was carried out on a dozen nanostructures per image to evaluate their mean dimensions (length and diameter) for each experimental condition. The growth direction of the nanostructures was characterized by imaging and selected area electron diffraction (SAED). The diffraction spots were indexed according to the JCPDS card No. 36-1452 of the tellurium hexagonal phase. The crystalline structure of the deposits was investigated by X-ray powder diffraction measurements (XRD, Bruker D8Advance) with Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 40 mA.

## 3. Results and Discussion

A typical cathodic linear voltammogram of Te<sup>IV</sup> in the piperidinium-based ionic liquid mixture is presented in Fig. 1.

We can observe two reduction peaks at –0.23 V (C<sub>1</sub>) and –1.2 V (C<sub>2</sub>) vs Pt reference electrode. The electrochemical behavior is the same as observed by Jeng et al [48], and Tsai et al [50], in imidazolium based ionic liquids. Consequently, the cathodic peak C<sub>1</sub> can be attributed to the reduction of Te<sup>IV</sup> into Te<sup>0</sup>, this latter being further reduced in Te<sup>-II</sup> at peak C<sub>2</sub>, according to [48,50]. This latter signal represents the cathodic limit for the deposition of Te<sup>0</sup> films [36]. It should be noticed that the shape of the cathodic linear voltammograms is the same whatever the tellurium salt concentration, exhibiting the C<sub>1</sub> and C<sub>2</sub> peaks. However the potential values of the peaks can vary in a 50 mV potential range.

### 3.1. Influence of Te<sup>IV</sup> concentration

The influence of Te<sup>IV</sup> concentration on Te electrodeposition was first studied at C<sub>1</sub> peak potential value (E<sub>p</sub>). Fig. 2 presents the SEM images of Te deposits obtained for a coulombic charge of 2C cm<sup>-2</sup> and [Te<sup>IV</sup>] = 25 mM (a), 20 mM (b) and 5 mM (c).

The results show unambiguously that the increase of the Te precursor concentration has a negative impact on the synthesis of low dimensional structures. For [Te<sup>IV</sup>] = 25 mM (Fig. 2a), corresponding to the maximal solubility of TeCl<sub>4</sub> in EOPipTFSI:EOPipBr 95:5 (mol%), the obtained deposit is dense, composed of nanostructures homogeneous in size of about 150 ± 20 nm in diameter but only 660 ± 50 nm in length. For [Te<sup>IV</sup>] = 20 mM (Fig. 2b), a

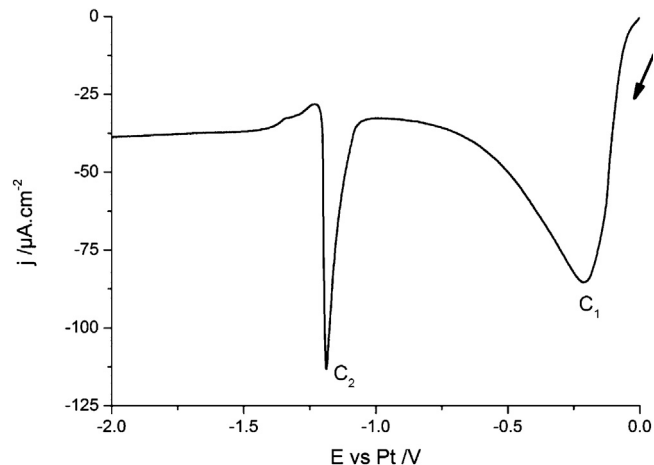


Fig. 1. Cathodic behaviour of Te<sup>IV</sup> in EOPipTFSI:EOPipBr 95:5 (mol%). [TeCl<sub>4</sub>] = 20 mM. Pt-coated glass slide substrate. T = 100 °C, scan rate 5 mV s<sup>-1</sup>.

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