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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 (1 D) 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.

Keywords: Electrodeposition, Nanowires, Tellurium, Ionic liquid, Hollow nanostructures

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 equation 1:

$$\text{Equation 1 } ZT = \frac{S^2 \sigma}{K_e + K_g} T$$

where S is the Seebeck coefficient, σ 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 membranes 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 $[\text{C}_2\text{mIm}][\text{BF}_4]/[\text{C}_2\text{mIm}]\text{Cl}$ [38]. Al nanowires were obtained by Su et al. in a Lewis acidic ionic liquid $\text{AlCl}_3/\text{trimethylamine hydrochloride}$ [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_4 . The authors show in this article that the capping agent is not here the ionic liquid but rather SiCl_4 that promotes the growth of Te nanowires. However, the use of SiCl_4 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

TeCl₄ (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; O₂/H₂O levels < 1 ppm). A mixture of EOPipTFSI and EOPipBr was used as electrolyte. EOPipBr improves the solubility of Te^{IV} 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^{IV} 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 cm². 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 K α radiation (λ = 1.5406 Å) at 40 kV and 40 mA.

3. Results and Discussion

A typical cathodic linear voltammogram of Te^{IV} in the piperidinium-based ionic liquid mixture is presented in Figure 1.

We can observe two reduction peaks at -0.23V (C₁) and -1.2V (C₂) 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 C₁ can be attributed to the reduction of Te^{IV} into Te⁰, this latter being further reduced in Te^{-II} at peak C₂, according to [48,50]. This latter signal represents the cathodic limit for the deposition of Te⁰ 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_1 and C_2 peaks. However the potential values of the peaks can vary in a 50 mV potential range.

3.1. Influence of Te^{IV} concentration

The influence of Te^{IV} concentration on Te electrodeposition was first studied at C_1 peak potential value (E_p). Figure 2 presents the SEM images of Te deposits obtained for a coulombic charge of 2 C.cm^{-2} and $[\text{Te}^{\text{IV}}] = 25 \text{ mM}$ (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 $[\text{Te}^{\text{IV}}] = 25 \text{ mM}$ (Figure 2a), corresponding to the maximal solubility of TeCl_4 in EOPipTFSI:EOPipBr 95:5 (mol%), the obtained deposit is dense, composed of nanostructures homogeneous in size of about $150 \pm 20 \text{ nm}$ in diameter but only $660 \pm 50 \text{ nm}$ in length. For $[\text{Te}^{\text{IV}}] = 20 \text{ mM}$ (Figure 2b), a compact deposit is obtained, composed of $1.0 \pm 0.1 \mu\text{m}$ long self-standing nanowires with a mean diameter of $140 \pm 20 \text{ nm}$, homogeneous in size. By decreasing the concentration at 5 mM (Figure 2c), longer nanowires are obtained, having a mean diameter of $130 \pm 20 \text{ nm}$ and a mean length of $1.2 \pm 0.2 \mu\text{m}$ corresponding to an aspect ratio of 9.2 ± 3.0 , the longest nanowires reaching $1.8 \pm 0.1 \mu\text{m}$. In these conditions, the nanowires are less homogeneous in size. One can also observe on Figure 2 that for $[\text{Te}^{\text{IV}}] = 5 \text{ mM}$, the array of nanowires is less dense than for higher concentration values, suggesting that the density of nuclei is smaller. This is in accordance with the electrocrystallization rules proposed by Scharifker and Hills [51].

SAED analyses were performed and typical diffraction patterns are displayed in the Figure 2, a, b and c. All the data exhibit single crystalline phase and the diffraction spots can be indexed to the hexagonal phase of tellurium (JCPDS card No. 36-1452). Whatever the concentration value, the corresponding zone axis is compatible with a growth direction along the c axis.

This result is in good agreement with the shapes of nanowires synthesized for $[\text{Te}^{\text{IV}}] = 5 \text{ mM}$, exhibiting a well-defined hexagonal shape.

Additional XRD crystallographic analyses of the deposits were performed (see Figure 3). The patterns reveal a preferential orientation along the [001] direction as discussed below.

Except the peaks related to the XRD sample holder and the Pt substrate, all the diffraction peaks can be indexed to the hexagonal phase of tellurium (JCPDS card No. 36-1452), confirming that the deposits are single phase. Sharpness of peaks suggests that the nanowires are well crystallized. In order to obtain a degree of preferential orientation, the Harris' texture coefficient (TC) was systematically calculated according to the following equation:

$$\text{Equation 2 } \text{TC}_{(hkl)} = \frac{\frac{I_{(hkl)}}{I_{(hkl)}^0}}{\frac{1}{N} \sum \frac{I_{(hkl)}}{I_{(hkl)}^0}}$$

where $I_{(hkl)}$ and $I_{(hkl)}^0$ are the measured intensity of a generic peak observed in the experimental XRD and the literature value from the data base (JCPDS card No. 36-1452), respectively, and N the number of diffraction peaks considered in the analysis. The TC results are presented in Figure 4.

Figure 4 shows that the texture coefficient of the (003) plane is higher than those of other (hkl) planes for Te^{IV} concentrations of 20 mM and 25 mM. These data corroborate the SEM images (Figure 2a and b), proving that the deposits are composed of dense and [001] oriented nanowires. The [001] orientation is due to the highly anisotropic crystal structure of tellurium(space group $P3_121$). In contrast, no marked orientation is observed for the deposits obtained at 5 mM, which can be explained by a random tilt of the nanowires on the substrate (Figure 2c).

3.2. Influence of applied potential

The influence of applied potential was studied for two concentration values: $[\text{Te}^{\text{IV}}] = 5 \text{ mM}$ (Figure 5 a-c), leading to the best aspect ratio at peak potential and $[\text{Te}^{\text{IV}}] = 20 \text{ mM}$ (Figure 5

d-f) for which dense arrays of nanowires were deposited. Three potential zones were tested: the half-wave potential value ($E_{1/2}$), corresponding to the potential where the current is half the C_1 peak current, the C_1 peak potential value (E_p), and a potential value (E_{diff}) more negative than E_p ($E_{diff}(V) = E_p - 0.15$). The deposits obtained at peak potential value previously presented in Figure 2 are reminded for easier comparison (Figure 5, b and e).

Whatever the concentration, the deposits obtained at $E_{1/2}$ are compact, composed of faceted micrometric grains (Figure 5, a and d). SAED analysis shows that these structures are single crystalline and grow preferentially along the [001] direction, as previously observed. One can see on Figure 5 that the diameter of the nanostructures decreases with applied overpotential; this phenomenon is more accentuated comparing the $E_{1/2}$ deposits and the E_p ones. This is in agreement with electrocrystallization principles, that is, the critical size of nuclei is inversely proportional to the deposition overpotential [52].

When the applied potential is much more negative than C_1 peak potential (Figure 5, c and f), the SEM observations of the deposits show of a compact sublayer composed of small grains and a mix of hollow nanostructures (HNs) and nanowires of several micrometers in length. It has already been shown that, using ionic liquids, HNs can be obtained in specific electrochemical conditions (Sn [40], CuZn [43] and $Cu_{10}Sn_3$ [53]).

One can also observe on Figure 5 that the amount of hollow nanostructures increases as the concentration of Te^{IV} decreases. This suggests that their formation results from an insufficient species supply. The formation of hollow nanostructures was already observed by Hsieh et al. when studying the synthesis of CuZn nanostructures by template-free electrodeposition [43], but, in their case, the reverse observation was made : HNs were obtained for low overpotential values under charge transfer control, whereas nanowires were obtained at higher overpotential when mass transport is controlling the growth.

In order to study the formation of HNs, ECD experiments were performed for different coulometric charge values (Q) at low Te^{IV} concentration (5 mM) and high overpotential (E_{diff}), corresponding to the same conditions as Figure 5c. Figure 6 presents the SEM and TEM images of the obtained deposits. As previously, a statistic study from the analysis of 1D nanostructures was carried out to determine their mean dimensions (length and diameter) as a function of Q . Corresponding values and calculated aspect ratio are presented in Figures 7a and 7b, respectively.

At 100 mC.cm^{-2} (Figure 6a), the deposit covers the entire working electrode surface and is composed of nanowires. When Q increases up to 200 mC.cm^{-2} (Figure 6b), some longer 1D nanostructures appear above a sublayer of smaller nanowires. This phenomenon is more and more pronounced as Q increases. One can notice that the nanowires are tip-shaped (inset of Figure 6b) and grow in diameter as fast as in length as shown in Figure 7a. Consequently, the aspect ratio remains constant, 10.0 ± 1.5 .

The first HNs appear for a coulometric charge of 400 mC.cm^{-2} (Figure 6c). By still increasing Q , the number of HNs increases (Figure 6, d-f), some of them being hexagonal shaped.

Lengths and diameters remain roughly proportional leading thus to the same aspect ratio as previously, 10.0 ± 1.5 (Figure 7a).

From the TEM images, it appears then that the nanostructures first grow as nanowires (Figure 6, a and b) and progressively turn into hollow nanostructures (Figure 6, c-f). Consequently, the structures are not hollow from one end to the other (see for example Figure 6, d-e). It seems then that there are several stages of growth: a first stage during which nanowires form, with a center part growing faster than the external parts, leading to tip-shaped structures, as was already observed in literature [34,54]. In the second part of the growth, 1D hollow nanostructures appear. According to Choi's [55,56] works, this formation might be due to a limitation by the diffusion of the precursor ions towards the center part of the growing

structures. This depletion zone formed in the central part of each structure leads to a faster growth of external parts, resulting in hollow structures formation. The formation of HNs was also observed during hydrothermal synthesis of Te nanostructures by Mayers and Xia [57]. The authors observed the formation of nanotubes when the supply in Te^{IV} precursor is rate-limiting whereas nanowires were formed otherwise.

The limitation by species supply seems then to favor the formation of HNs as the coulometric charge increases. To justify this assumption, additional experiments were conducted by using a Te soluble anode as counter electrode in the experimental conditions leading to HNs formation, namely a low tellurium salt concentration (5 mM) and a high overpotential (E_{diff}). A typical deposit is presented in Figure 8.

One can observe on Figure 8 that only nanowires are formed. As opposite to the experiments conducted in the same growth conditions without the use of a soluble anode (see Figure 6f), no HNs are noticed. Using a soluble anode, the concentration of Te^{IV} in the electrolyte is supposed to be constant during the electrolysis. This hypothesis is based on the presence of the anodic peak corresponding to $\text{Te}(0)$ dissolution, observed by Szymczak et al. in the same electrolyte [49]. Consequently, the diffusion layer thickness remains constant during the whole experiments leading to constant diffusion flux.

Obtained nanowires are not very homogeneous in size and their density is low. However, the mean length is $5.0 \pm 2.0 \mu\text{m}$ whereas without the use of a soluble anode, it is of $2.7 \pm 1.0 \mu\text{m}$. The mean diameter remains the same that previously observed, $250 \pm 100 \text{ nm}$. The use of a soluble anode allows then to obtain NWs instead of HNs, with larger length and equivalent diameter. Thus this additional result confirms that the growth of HNs is related to species supply.

The conducted experiments in this work show that the origin of the nanostructuration (NWs and HNs) is governed by the applied overpotential and the cationic concentration. It should be

noted that, from the literature data [36–45], ionic liquids could play the role of capping agents. Besides, halide anions can also be responsible of the growth of nanostructures as observed by Al-Salman et al. [35]. In our work, it is difficult to discriminate between halide effect and IL ions effect, as the only Te(IV) salts that are soluble in TFSI-based ionic liquids are halide salts.

4. Conclusions

In this work, we have shown that it is possible to control the shape and the size of the deposited nanostructures by varying the experimental parameters that influence the deposition kinetics. It appears in particular that the applied potential has a very strong influence on the deposit morphology. Under charge transfer control, micrometer faceted grains are observed. Under diffusional control, the deposits are composed of nanowires. In high overpotential conditions, nanowires turn progressively into hollow nanostructures due to a limitation by species supply. This phenomenon is more accentuated at low concentration.

This work shows that Te nanowires of high crystallinity can be obtained by electrodeposition in ionic liquids. They could be used as starting materials for the synthesis of core-shell structures. Hollow nanostructures synthesized in specific conditions are also interesting to create high performances thermoelectric materials. Indeed, this geometry could further decrease the lattice part of the thermal diffusion coefficient by phonon confinement.

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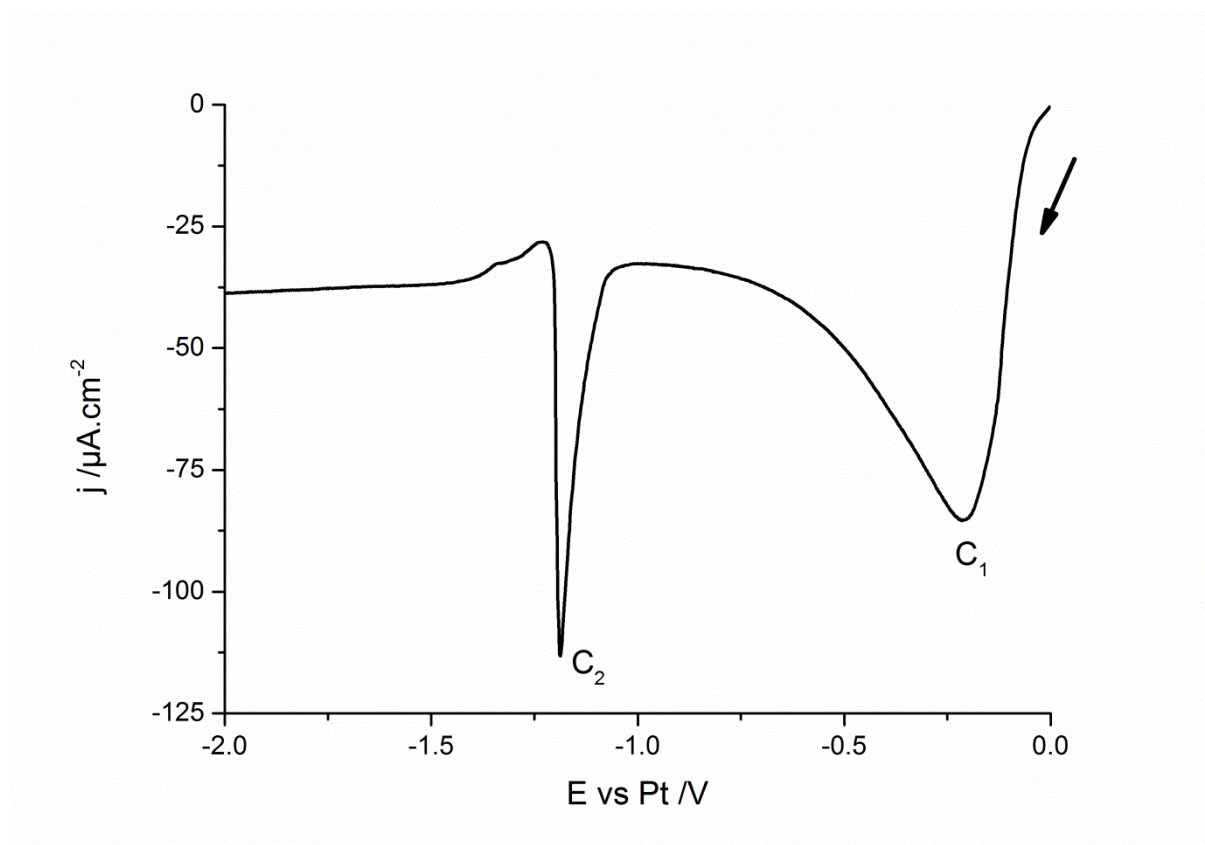
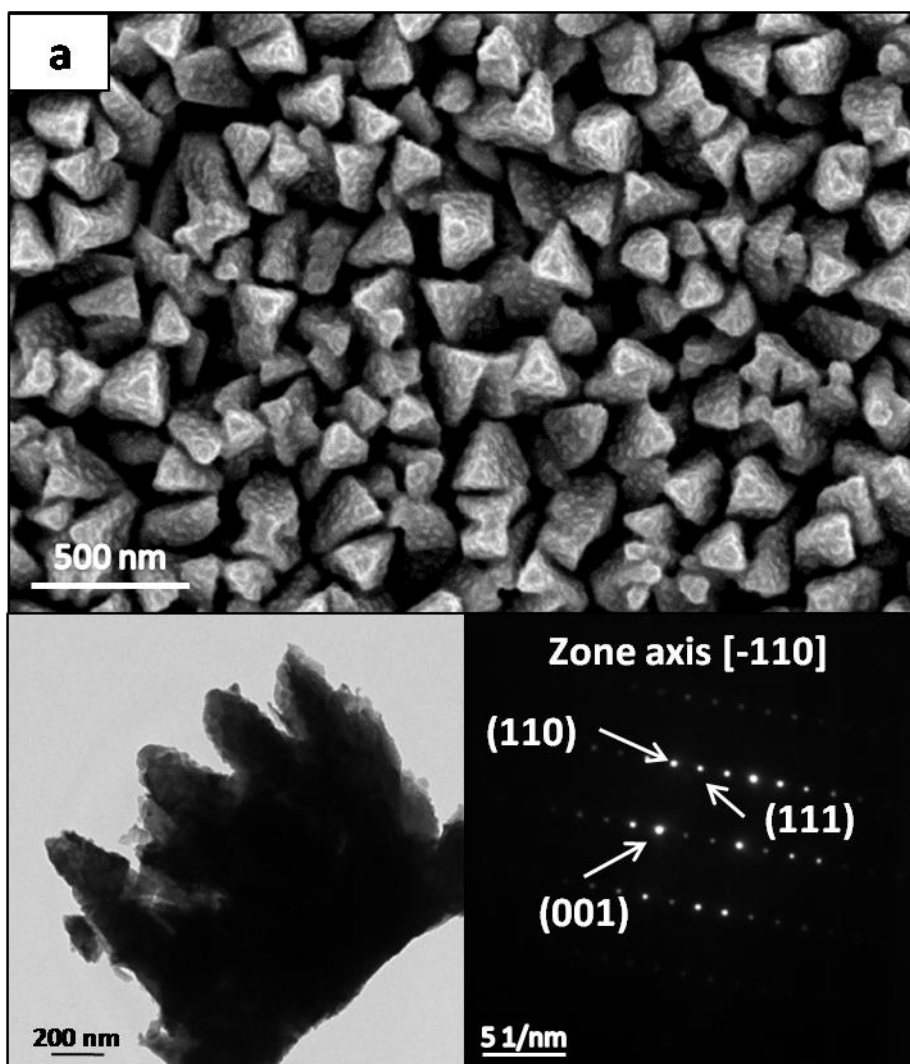


Figure 1: Cathodic behaviour of Te^{IV} in EOPIpTFSI:EOPIpBr 95:5 (mol%). $[\text{TeCl}_4] = 20 \text{ mM}$.

Pt-coated glass slide substrate. $T = 100^\circ\text{C}$, scan rate 5 mV.s^{-1} .



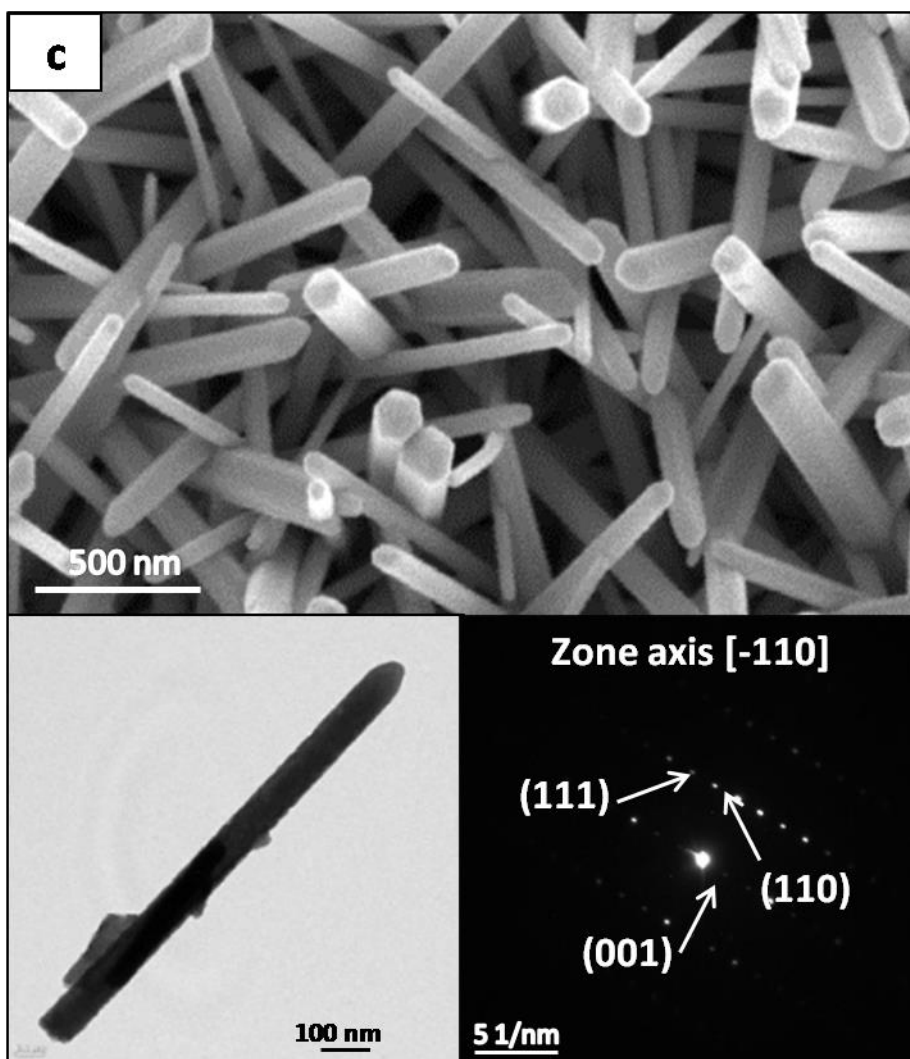


Figure 2: SEM images of Te nanostructures electrodeposited at $E_{\text{dep}} = E_p$ in EOPipTFSI:EOPipBr 95:5 (mol%) containing $[\text{Te}^{\text{IV}}] =$ (a) 25 mM, (b) 20 mM and (c) 5 mM. $T = 100^\circ\text{C}$, $Q = 2 \text{ C.cm}^{-2}$, Pt-coated glass slide, 0.5 cm^2 . Insets show corresponding TEM images and SAED diffractograms (the diffraction spots are indexed to the tellurium phase CPDS card No. 36-1452).

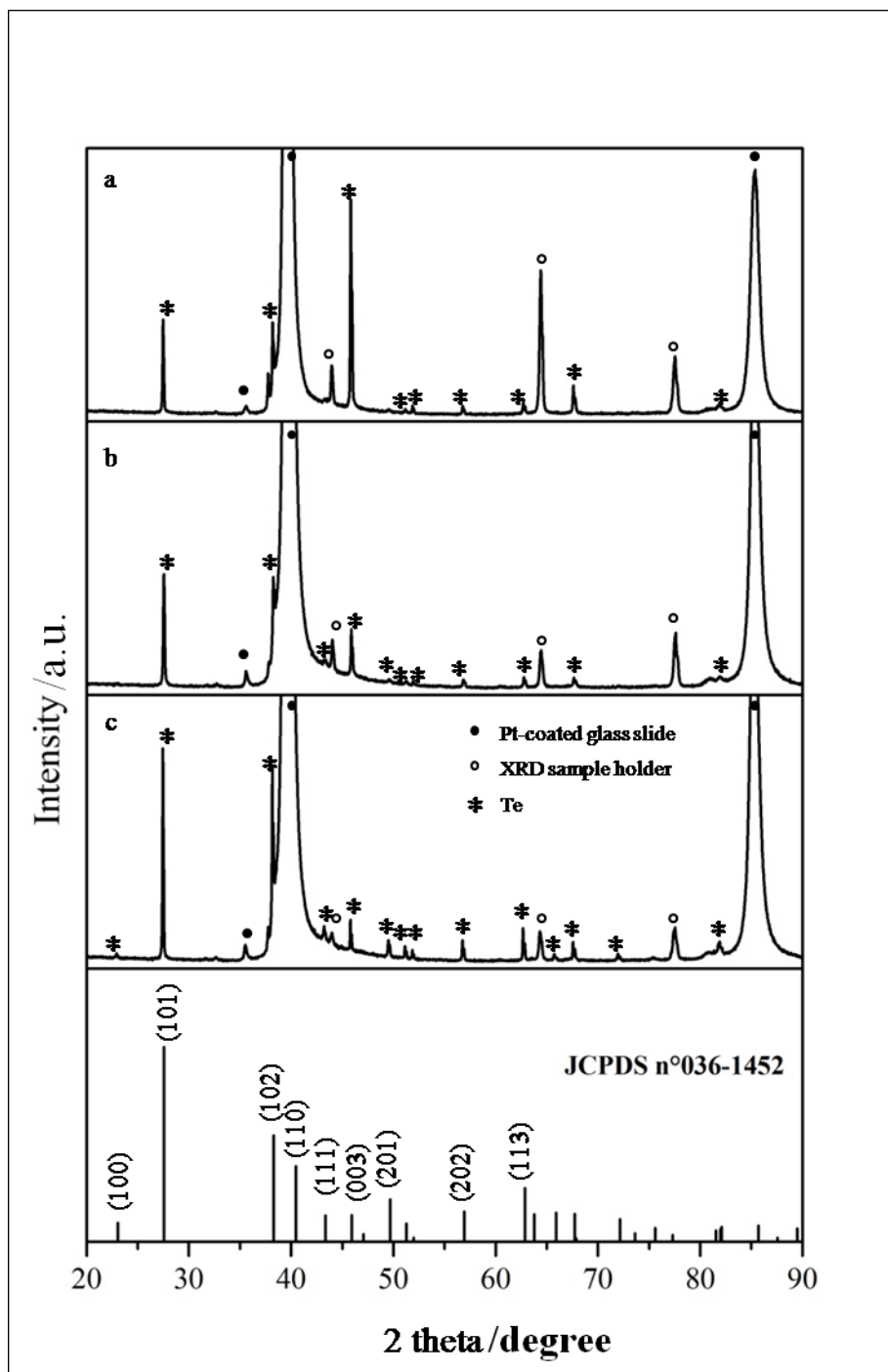


Figure 3: XRD pattern of a Te deposit

Pt-coated glass slide, $[\text{Te}^{\text{IV}}] =$ (a) 25 mM, (b) 20 mM and (c) 5 mM.

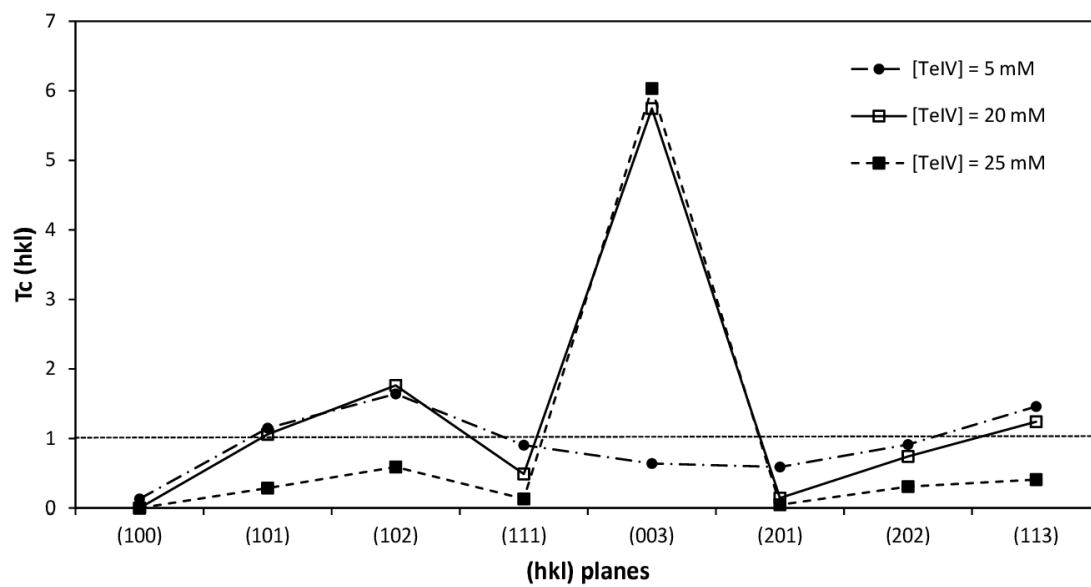


Figure 4: Texture coefficients of tellurium nanowires according to (hkl) planes, calculated from XRD data presented in Figure 3

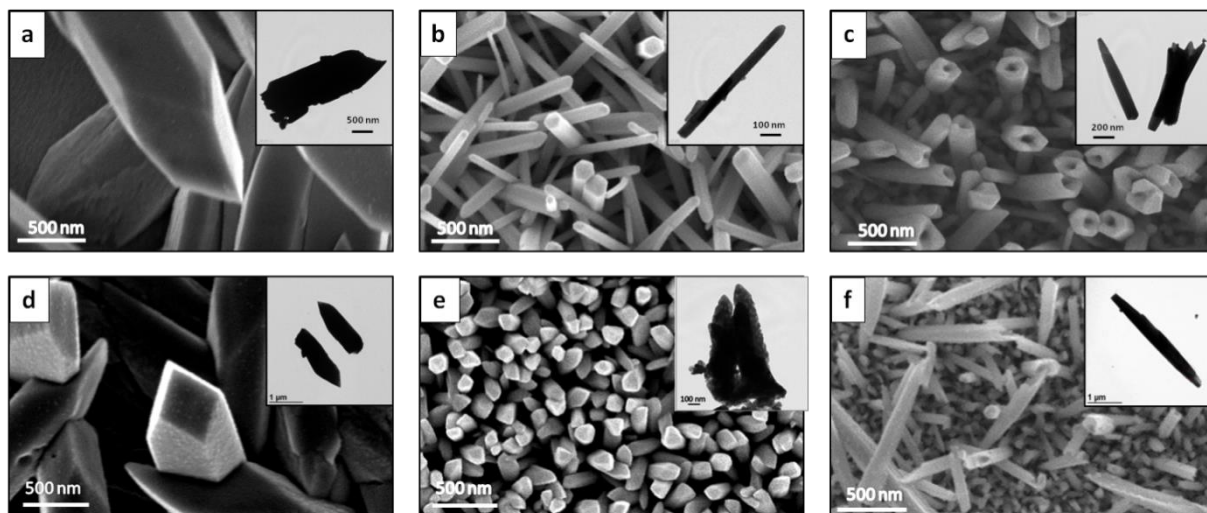


Figure 5: SEM images of Te nanostructures deposited in EOPIpTFSI:EOPIpBr 95:5 (mol%) for different applied potential values. $T = 100^{\circ}\text{C}$, $Q = 2 \text{ C.cm}^{-2}$, Pt-coated glass slide. Insets show the TEM images.

$[\text{Te}^{\text{IV}}] = 5 \text{ mM}$: (a) $E_{1/2}$, (b) E_p and (c) E_{diff} ; $[\text{Te}^{\text{IV}}] = 20 \text{ mM}$: (d) $E_{1/2}$, (e) E_p and (f) E_{diff}

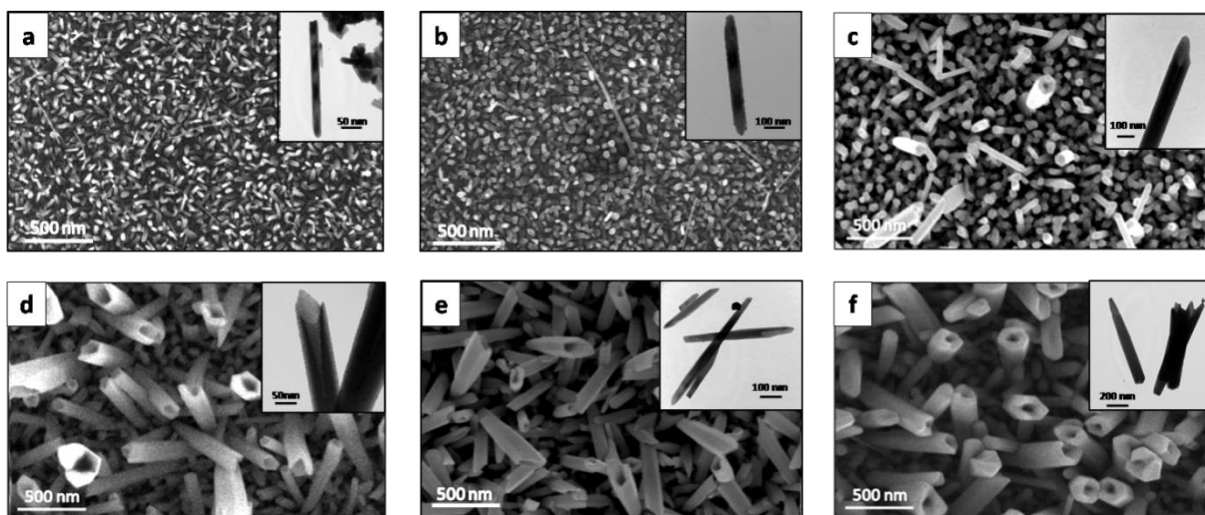


Figure 6: SEM images of Te nanostructures electrodeposited for different coulometric charge values in EOPipTFSI:EOPipBr 95:5 (mol%), $E_{\text{dep}} = E_{\text{diff}}$, $[\text{Te}^{\text{IV}}] = 5 \text{ mM}$, (a) 100 mC.cm^{-2} , (b) 200 mC.cm^{-2} , (c) 400 mC.cm^{-2} , (d) 800 mC.cm^{-2} , (e) 1 C.cm^{-2} and (f) 2 C.cm^{-2} , $T = 100^\circ\text{C}$, Pt-coated glass slide

Insets show the TEM images of Te nanostructures.

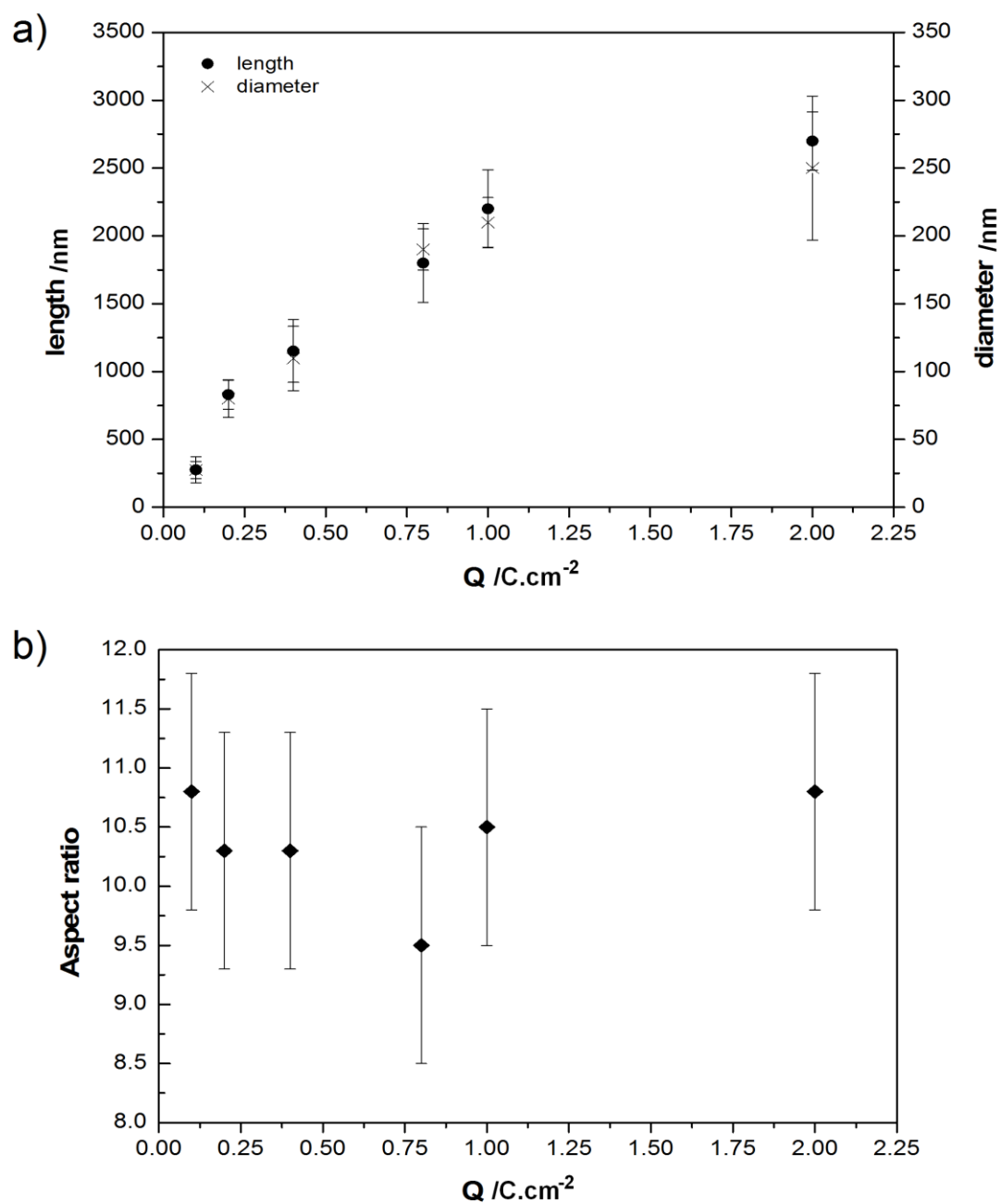


Figure 7: Evolution of a) length and diameter and b) aspect ratio of Te one-dimensional

nanostructures according to applied coulometric charge value, $[\text{Te}^{\text{IV}}] = 5 \text{ mM}$, $E_{\text{dep}} = E_{\text{diff}}$

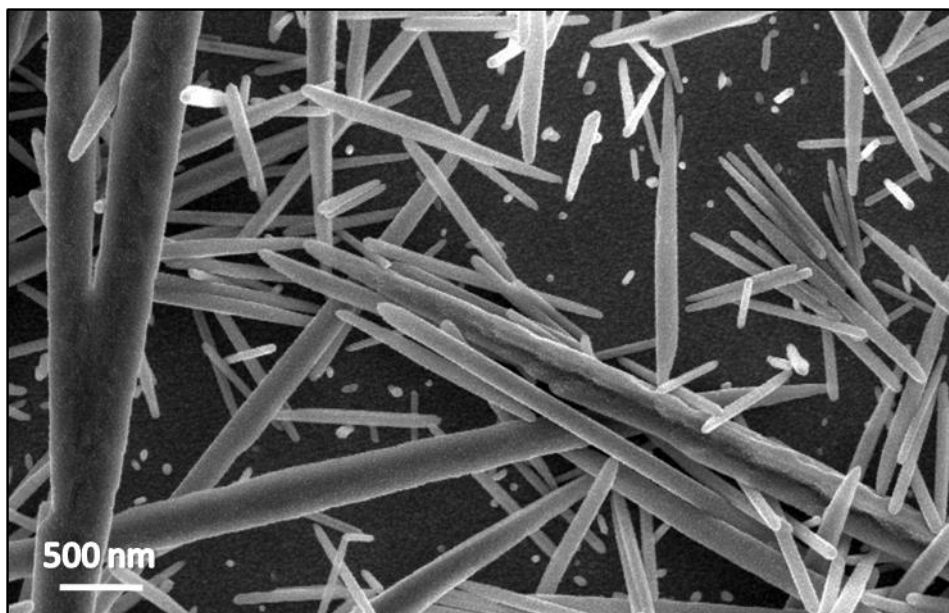


Figure 8: SEM images of Te nanostructures electrodeposited with a Te soluble anode in EOPipTFSI:EOPipBr 95:5 (mol%), $E_{\text{dep}} = E_{\text{diff}}$, $[\text{Te}^{\text{IV}}] = 5 \text{ mM}$, $T = 100^\circ\text{C}$, $Q = 2 \text{ C.cm}^{-2}$, Pt-coated glass slide.