

STUDY OF THE MORPHOLOGY OF TeO₂ MICRORODS BY SOLVOTHERMAL METHOD

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In this work, the influence of polyvinylpyrrolidone (PVP) in the growth of tellurium oxide synthesized by solvothermal method is studied. The materials used were sodium tellurite (Na₂TeO₃), trimethylamine (N(CH₂CH₃)₃), ethylene glycol (C₂H₆O₂), and different amounts of polyvinylpyrrolidone ((C₆H₉NO)_n). The growth of TeO₂ showed a large variation in morphology depending of the amount of PVP. The materials presented a growth in form of microrods for the amount of 0.4 grams of PVP, to larger amounts of 0.6 grams of polymer began to present a deformation in morphology. The analysis of materials by FTIR showed a bond Te-O at a frequency of 520-680 cm⁻¹, this bond is characteristic of tellurium oxide (TeO₂).

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1. Introduction

Tellurium oxide has a wide range of applications in technology such as deflector [1], modulators [2], dosimeters [3], optical storage materials [4], laser devices [5] and gas sensors [6], due to its physical and chemical properties, including excellent optic-acoustic properties adequate to those applications [7]. In the literature, there have been reported a variety of methods for the preparation of materials such as: sputtering technique [8], melt-quenching method [9], chemical vapor deposition [10], solvothermal method [11], and the solvothermal method has shown significant advantages over the other methods, due to is easy, simple, flexible, with a general process and it is profitable without a catalyst and template, and it could be applied to a wide range of nanostructures which have diverse chemical compositions [12,13]. It is well known that with the development of the science and technology, the field of materials growth in diverse conditions, it has received considerable attention. The above has been an incentive in the study of materials trying to determine the behavior of them at different parameters: temperature [14], pressure [15], and concentration [16]. To our knowledge, there is no previous report about the study of the growth of tellurium oxide using variable amounts of PVP. In this work, the effect of the amount of PVP on the growth of tellurium oxide by the solvothermal method is reported.

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2. Experimental

The reagents used were analytical grade and were prepared with the following procedure, 0.5 mL of triethanolamine (TEA) and 12 mL of ethyleneglycol (EG) were put in an teflon coated autoclave of 30 mL vol. Immediately, 0.05 g of Na_2TeO_3 and different amounts of PVP (0.2, 0.3, 0.4, 0.5, 0.6, and 1.0 grams), were added inside the autoclave and maintained with stirring for 1 hour. After that a clear solution was formed which one was sealed in a stainless steel container and putting in an furnace at 175 °C for 10 h without stirring. After the thermal treatment, the autoclave was allowed to stand at room temperature for a lapse of 12 hours inside the furnace. The reaction products were centrifuged at 12000 rpm, washed several times with deionized water and absolute ethanol, respectively, and then dried in oven at 65 °C during 24 h. The materials characterization was performed by means of a Jeol JSM-5300 SEM integrated with an energy analyzer for electron scattering ThermoNoran for the study of morphology and chemical composition. Fourier transformed infrared spectrometry was used to determine the vibrations of the functional group of the tellurium oxide prepared with different amounts of PVP.

3. Results and discussion

The surface analysis of the synthesized materials for the solvothermal method, with different amounts of polyvinylpyrrolidone (PVP), was done through scanning electronic microscopy, as shown in Figure 1. The results for the sample with an amount of PVP = 0.2 grams, revealed microrods with a long of 12 ± 2 microns, these results are very similar to those reported by Filippo [17], where they synthesized their material using the thermal evaporation method, obtaining microrods with bigger diameter than those prepared by us, as presented in Figure 1(a). For the sample with 0.3 grams of PVP it was observed a distribution with microrods of the same length that the above samples but with a thicker morphology (Figure 1(b)), in these samples it is possible appreciate microrods sets of approximately 2 microns of thickness, this could be due to an excess of PVP, which produce an agglomeration of the oxide. On the other hand, the sample with 0.4 grams of PVP presented agglomerations with lengths not very well defined and broken sections. The microrods that this material exhibited were smaller than the above microrods belonging to the samples with 0.2 and 0.3 grams of PVP (Figure 1(c)). The results for the amount of 0.6 grams of polymer (Figure 1(d)), displayed an agglomeration of microrods without any direction with broken materials with small length in comparison with the former samples, this fact permitted us conclude that in amounts bigger than 0.4 grams of PVP, the morphology of the microrods is agglomerations of this material losing the defined form presented in samples with less amounts of polymer. Therefore, the PVP plays a very important role in the growth mechanism of the microrods. As it is shown in Figure 2 where is presented a scheme proposing this mechanism of growth of this materials; starting with tellurium oxide particles which ones are putting in contact with the polymer then they are surrounded by the polymer but the particles grow unidirectionally forming the microrods, this fact is more notorious when the amount of PVP is increasing according with the observations trough SEM. The above, could be due to that the polymer attract the TeO_2 and can directs the growth of the microrods and the thickness. Similar results for this type of materials were presented previously by Park [18].

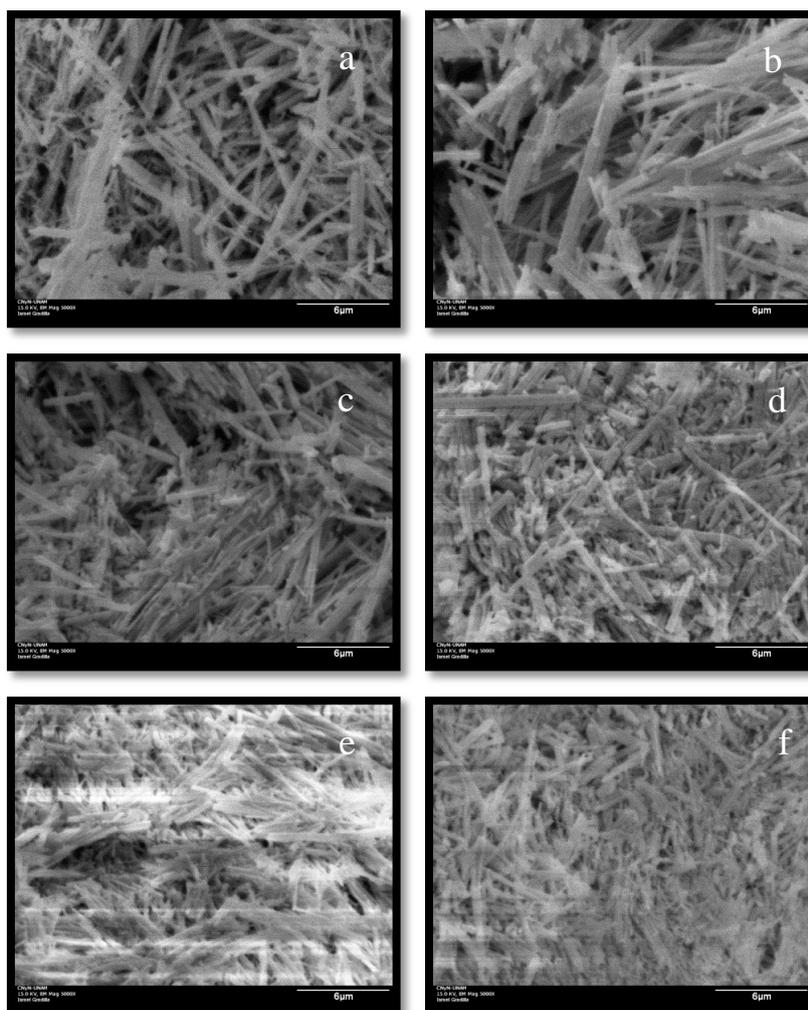


Fig. 1.- Effect of PVP on TeO_2 : a) 0.2g, b) 0.3 g, c) 0.4 g, d) 0.5 g, e) 0.6 g and f) 1.0 grams

Fig. 3 shows the results of Fourier transformed infrared spectrometry. The analysis was done in a frequency range of $520\text{-}2500\text{ cm}^{-1}$ at room temperature. The results show a strong band in $520\text{-}680\text{ cm}^{-1}$, this signal is characteristic from the Te-O bond, which one confirm that the material is tellurium oxide (IV) [19]. Also, it is possible to observe that in samples synthesized using amounts bigger than 0.4 grams of PVP this signal decrease that could be due to the morphology inhomogeneous of these materials.

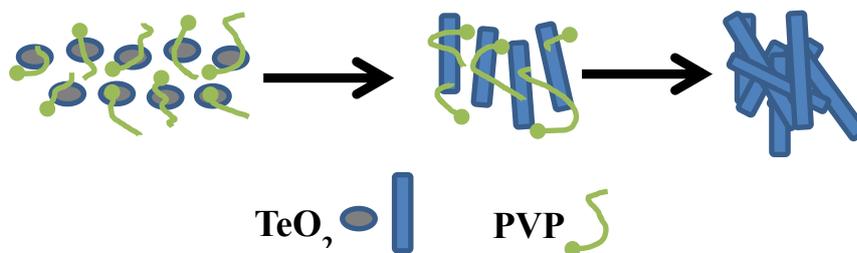


Fig. 2. Scheme of the tellurium oxide growth mechanism.

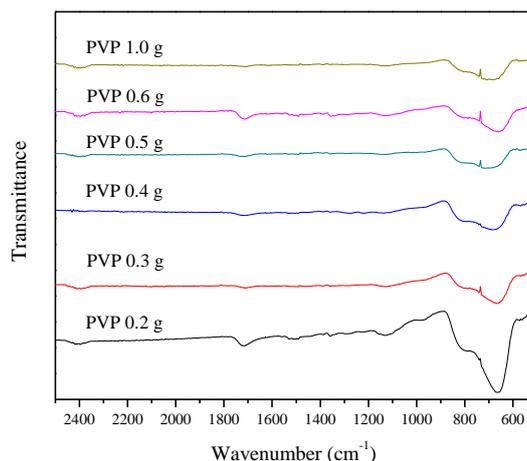


Fig. 3.- FTIR graph of samples synthesized with different amount of PVP

The analysis of percentage composition was realized through energy dispersive spectrometry of ray-X (EDX). In Figure 4, one can observe the characteristic spectra of EDX, where the presence of tellurium and oxygen is visible; moreover all the materials presented almost the same proportion of Te/O, with a variation of the 5 %. These results are similar to those reported in the literature by Siliciano [20], but within their results there are signals of aluminum, due to they used the Al as substrate probably. In this EDX analysis, it can be seen that there is no presence of reaction residues, neither of the material precursors, nor solvents, and this fact can be corroborated with the results obtained by SEM, where no particles are observed around the rods synthesized by the solvothermal method.

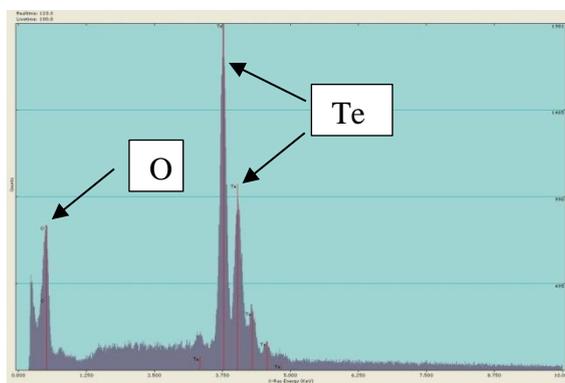


Fig. 4.- EDS of the tellurium oxide.

4. Conclusions

Microrods of tellurium oxide were prepared via the solvothermal method using different amounts of PVP. The study of the morphology of the materials show that the tellurium oxide presented differences in function of the amount of PVP, with a predisposition to the formation of microrods with different lengths and thickness. The synthesized materials presented more homogeneity for amounts of PVP of 0.2 and 0.3 grams than for larger amounts of PVP which ones presented agglomerates and brittle microrods. The materials were identified via FTIR spectra which ones showed a signal for the bond of this type of samples and were corroborated by the EDX technique, in their results possible contaminants reaction products were not observed.

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