Synthesis and characterisation of electrospun poly (ethylene oxide) nanofibers enriched with VO_2 nanoparticles for the development of unidimensional nanomaterials

Síntesis y caracterización de nanofibras de óxido de polietileno enriquecidas con nanopartículas de VO_2 por la técnica de *electrospinning* para el desarrollo de nanomateriales unidimensionales

Rodríguez-Zamora, P.,*[1] Simo, A.,[1] Khamlich, S.,[1] McDonald, E.,[2] Peterson, N.,[2] Maaza, M.[1]

[1] iThemba Laboratory for Accelerator Based Sciences, Somerset West 7129, South Africa
[2] University of the Western Cape, Bellville Robert Sobukwe, Cape Town, South Africa
*e-mail: penelope.rodriguez.zamora@gmail.com

Technological innovation: New nanomaterials based on polymer fibers.

Industrial application area: Industry of electrochromic materials and biomaterials.

Resumen

Nanofibras de óxido de polietileno enriquecidas con óxido de vanadio fueron producidas primeramente realizando la síntesis de nanopartículas de VO_2 por reducción de V_2O_5, seguido de la generación de fibras por la técnica de *electrospinning* a partir de la solución PEO-VO_2. La estructura cristalina de las nanopartículas de VO_2 fue comprobada por difracción de rayos X. La morfología, estructura y las propiedades de transmisión de energía infrarroja de las nanofibras híbridas fueron caracterizadas por difracción de rayos X, microscopía de electrones por barrido, microscopía de transmisión de electrones y espectroscopía de transformada de Fourier del infrarrojo. Exhibimos que la morfología de las fibras de PEO no se modifica por la presencia de VO_2 debido al incorporamiento de las nanopartículas dentro de las fibras durante el proceso de *electrospinning*. Una interacción de enlace entre PEO y VO_2 que no distorsiona la estructura semicristalina de PEO fue confirmada a través de un análisis vibracional del compuesto. Esto demuestra que la incorporación de las propiedades termocrómicas de VO_2 y la simultánea conservación de la cristalinidad de PEO puede ser lograda para nanocompuestos unidimensionales, a diferencia de los materiales bidimensionales de PEO-VO2 análogos. La técnica de síntesis que presentamos en este trabajo ha probado ser viable para la fabricación de nanocompuestos híbridos (polímero/óxido de metal) unidimensionales con aplicaciones potenciales en medios ópticos de almacenamiento de datos, cubiertas funcionales termocrómicas y baterías de litio y magnesio para dispositivos móviles y vehículos eléctricos.

Palabras clave: electrospinning, nanofibras, dióxido de vanadio.

Abstract

Poly (ethylene oxide) nanofibers doped with vanadium dioxide were produced by firstly synthesising VO_2 nanoparticles by V_2O_5 reduction followed by electrospinning of the PEO-VO_2 polymer solution. The crystalline structure of the VO_2 nanoparticles was ascertained by X-ray diffraction. The morphology, structure and molecular vibrational properties of the hybrid nanofibers were characterised by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and Fourier transform infrared spectroscopy. We exhibit that the morphology of the PEO nanofibers is not modified by the addition of VO_2 due to the embedment of the nanoparticles within the polymer during the process of electrospinning. A bonding interaction between the PEO and the VO_2 that does not disrupt the semi-crystalline structure of PEO was confirmed by vibrational analysis of the composite. This demonstrates that incoporation of the VO_2 thermochromic properties to PEO and simultaneous conservation of crystallinity of the polymer can be achieved for unidimensional nanocomposites, contrary to the case of the PEO-VO_2 bidimensional analogous materials. The synthesis approach that we present in this work has proved to be viable for the fabrication of one-dimensional polymer/metal oxide hybrid nano-composites with potential applications in optical data storage media, thermochromic functional coatings and in lithium and magnesium batteries for mobile devices and electric vehicles.

Key Words: electrospinning, nanofibers, vanadium dioxide.

1. Introduction

Different studies and applications have demonstrated in the last decades the advantages of unidimensional materials [1, 2]. In particular one-dimensional nanostructures (ODNS) have attained significant attention in nanoelectronics, nanodevices, nanocomposite materials, and alternative energy resources, with an important impact in the development of technology in all the mentioned fields [3]. The explanation for such success relies on the physical characteristics that differ in certain materials from one dimension to the other within the nanoscale. In one dimension, materials have a very large surface area to volume ratio, which gives them unique quantum properties, resulting in new electronic possibilities [4]. 1D nanostructures also have a superior mechanical performance compared to their 2D counterparts, for example stiffness and tensile strength [5].

Polymers [6] and in particular polymer nanofibers (Nfs) haven shown higher flexibility, tunable porosity and other surface functionalities, properties that make them ideal candidates for a wide variety of applications [7]. One of the most commonly used techniques to produce polymeric nanofibers is electrospinning.

The electrospinning technique is capable of generating nanofibers with diameter of hundreds to tens of nanometers with ease of functionalisation for various purposes and in large-scale production [8]. The physical principle is based on an electric field produced by a high voltage supplier that creates a charged jet of polymer solution through a capillary tube. By increasing the intensity of the electric field, the droplet at the tip of the capillary tube elongates leading to the formation of a conical shape known as the Taylor cone [9]. When the repulsive electrostatic force overcomes the surface tension the fluid is ejected from the tip of the Taylor cone [7]. As this jet travels from the emitter to the collecting screen, the solution evaporates creating a charged fiber that is electrically deflected [10].

Depending mainly on the polymer molecular weight, the viscosity of the polymeric solution and the voltage applied to the electrospinning system it is possible to generate fibers with different cross sectional shapes and sizes [11]. It is also possible to combine materials with different properties in order to achieve maximum efficiency according to each application at the time of ensuring cost effectiveness [8].

The combination of different polymers (e.g. PEO, PVP, PEG) with metal and metal oxide nanoparticles (NPs) has been explored within the research fields of transport membrane [12]; biosensing [13]; and transparent conductors [14] among other varied areas.

In particular, the coupling of PEO with VO_2 nanoparticles to form bidimensional structures has gained interest due to its enhanced thermochromic [15] and electrical properties, including high conductivity [16] and charge storage [17], and has been tested for application in high energy lithium and magnesium batteries, chemical sensors [18] and optoelectronic devices [19].

The above cases are examples of hybrid two-dimensional composites, such as thin films and xerogels. In this paper we explore the synthesis of a one-dimensional organic-inorganic hybrid material formed by PEO electrospun nanofibers enriched with VO_2 NPs. We attain to explore the possibilities for new one-dimensional nanomaterials that incorporate the high stability and good ionic conductivity of PEO and the electrochromic and thermochromic properties of VO_2 [20] for applications in electronic devices, thermochromic sensors, energy and data storage and biomedical applications [21].

We used XRD, SEM, HR-TEM and FTIR in order to ascertain the modifications in characteristics that the presence of metal oxide NPs infer in the polymeric fibers and whether or not the NPs properties are conserved once combined with the nanofibers.

2. Experimental details

2.1 VO_2 nanoparticles synthesis

VO_2 NPs were synthesised by Dr. Simo by reduction of V_2O_5 (*Sigma-Aldrich*) with oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) (*Sigma-Aldrich*) as a reducing agent. Both reactants, in 1:2 molar ratio, were added directly into 20 ml ddH_2O at room temperature. The suspension was continuously stirred until a clear black-blue solution was formed and then transferred into a Teflon-lined autoclave. The hydrothermal treatments for the solutions were carried out at temperature ranges from 180 to 230 °C at a filling ratio of 0.40, and holding for 24 h. After hydrothermal treatment, the autoclave cooled naturally to room temperature. The resulted precipitates were collected by filtering, washed with ddH_2O and ethanol several times, then dried in air at 60 °C for 10 h.

2.2. PEO-VO_2 nanofibers synthesis

2.5 g of 300,000 molecular weight Poly (ethylene oxide) (PEO) (*Sigma-Aldrich*) were added to 100 ml of methanol for a concentration of 83 mM. The solution was stirred overnight at room temperature in order to obtain the necessary viscosity for electrospinning (1-20 poise [22]). The electrospinning system setup used (*ElectropinTech-Spraybase,* at iThemba LABS) consisted of an emitter of 0.9 mm diameter, an aluminium collection surface electrically grounded and an emitter-collection surface distance of 10 cm. 5 ml of PEO solution were loaded in the system using a 5cc syringe and a voltage of 10 kV was applied for a deposition time of 30 min at a rate 0.3 ml/hr in order to obtain PEO Nfs. A second PEO solution with the same concentration was produced, from which 10 ml were enriched with 20 mg of VO_2 NPs synthesised by our research group. The VO_2 NPs powder was homogenised using a

mortar until getting a finer powder, which was then added to the PEO solution. Electrospinning procedures and parameters for this second solution were the same as before.

2.3 Characterisation

The VO$_2$ NPs were characterised by the X-ray diffraction system of the Materials Research Department (MRD) at iThemba LABS and the scanning electron microscope (SEM) *Bruker-EDS* of the Physics Department at the University of Western Cape (UWC). Polymeric Nfs with and without the presence of NPs were morphologically and structurally characterised by X-ray diffraction, SEM, as well as by high resolution transmission electron microscopy (HR-TEM) *Tecnai F20* equipped with ETS, STEM, EELS and HAADF systems (UWC). Infrared transmission properties were determined by a *Perkin Elmer Spectrum Two* system of Fourier transform infrared spectroscopy (FTIR) (UWC).

3. Results and discussion

3.1 PEO nanofibers synthesis

The electrospinning required viscosity for PEO-methanol solution was obtained on the first attempt, facilitating the work with this particular polymer and demonstrating the advantages of it in the production of electrospun Nfs. The Taylor cone, precursor of successful Nfs, was formed at the end of the emitter at 10kV, generating enough electrostatic force on the surface of the solution to overcome the surface tension and producing a thin jet with solvent evaporation which resulted in a continuous flux of electrospun PEO Nfs. Deposition was carried out on a glass slide substrate previously cleaned with methanol, water and dried with nitrogen gas. The deposition time was 1 hr, after which we obtained an homogeneous film (Fig.1).

3.2 VO$_2$ NPs structural characterisation

Crystal structure of VO$_2$ NPs was confirmed by XRD (Fig.2) showing a structure in agreement with the pattern corresponding to the crystalline characteristic diffraction peaks of vanadium (IV) dioxide. All peaks can be indexed as the monoclinic phase, space group P2$_1$/c that correspond to the crystalline structure of VO$_2$ at room temperature and below 70 °C [23, 24]. This corroborated that the experimental conditions for the synthesis of the NPs were optimal for the reproducible production of VO$_2$ by reduction of V$_2$O$_5$.

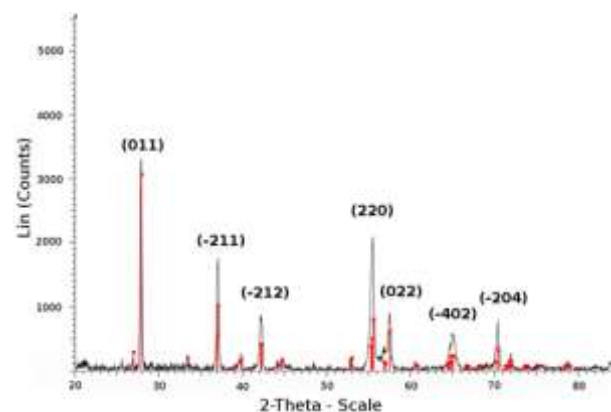**Figure 1.** Photography of PEO electrospun Nfs deposited on glass substrate.

Figure 2. XRD diffractogram of VO$_2$ NPs. Comparison between experimental diffraction peaks obtained from the VO$_2$ NPs powder (black) and theoretical values for the VO$_2$ crystal structure (red) indicating the correspondent crystalline planes [24] for the strongest peaks.

The NPs were also analysed using SEM which images revealed particles with rectangular prism shape with a parallelogram as base and unequal vector lengths that confirm the expected monoclinic crystal structure corresponding to VO_2. The size distribution showed an average base length of 100 nm and a longitudinal average dimension of 600 nm (Fig.3).
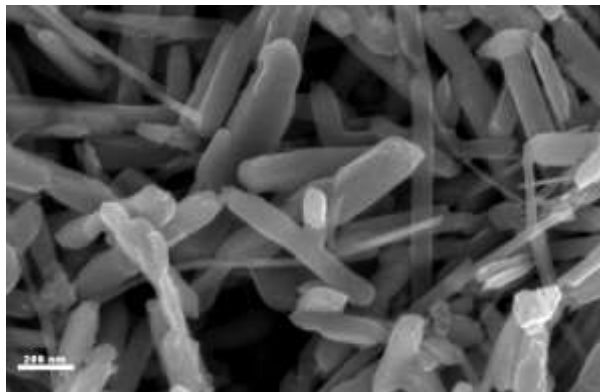

Figure 3. Scanning electron microscopy images of VO_2 NPs.

3.3 PEO-VO_2 Nfs synthesis and characterisation

Electrospinning production

Synthesis of the hybrid Nfs was made following the same procedure of polymer solution as for pure PEO fibers. During the first hours of stirring after incorporation of the powder, the VO_2 NPs started to dissolve in the polymer solution, therefore changing the colour of the latter from white to grey. Although the incorporation of the NPs was highly homogeneous, some larger powder particles remained undissolved. The mixed solution was used to produce PEO-VO_2 Nfs by electrospinning with the same deposition parameters as for the pure PEO Nfs, demonstrating that the presence of VO_2 did not affect the propensity of PEO to form fibers easily by the electrospinning technique.

X-ray diffraction characterisation

X-ray diffraction measurements were carried out for the pure PEO Nfs produced by electrospinning obtaining peaks at $2\Theta=$ 19.1° and 23° in respective correspondance with the (120) and (032) reflection planes of the PEO monoclinic crystalline phase [25, 26]. XRD data was also obtained from the PEO-VO_2 Nfs sample (Fig.4), which reproduced the PEO difractogram, reflecting the low relative concentration of VO_2 in the sample. However, the PEO-VO_2 difractogram demonstrated a clear increment on the signal with respect to the pure PEO diffraction peaks, especially at $2\Theta=23°$. Smaller peaks at $2\Theta=$ 13.5, 14.5, 15, 21.4, 26, 27.5, 36 degrees are also stronger in the sample containing VO_2. The absence of peaks corresponding to the crystal structure VO_2 reveals that the hybrid fibers do not inherit the crystalline properties of the VO_2 NPs, potentially pointing to an embedment of the NPs in the polymer fibers. However, XRD results demonstrated that the natural semi-crystalline structure of PEO is not disrupted by the addition of VO_2 NPs as it is the case for bidimensional PEO-VO_2 nanocomposites [16, 17].
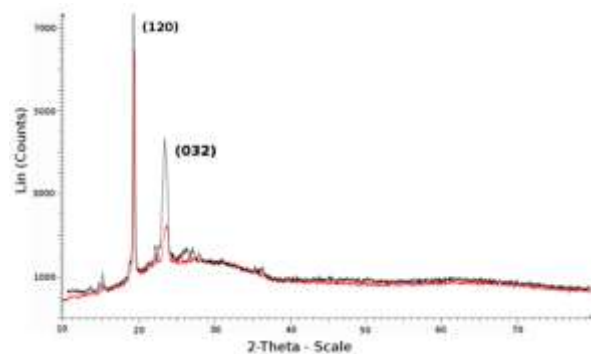

Figure 4. XRD diffractogram of pure PEO electrospun Nfs (red) and hybrid PEO-VO_2 electrospun Nfs (black) indexed according to the crystalline phase of PEO [25].

Electron microscopy characterisation

Scanning electron microscopy (SEM) was used on a pure PEO Nfs sample first to ensure that the visible film formed after

deposition consisted of fibers and that the production of these by electrospinning was successful. It can be seen that the fibers have random orientation and different longitudinal lengths with high continuity, both characteristics combined to form a dense net of fibers in multilayers. It is possible to distinguish between fibers with unequal diameter, being the ones with longer diameter (average length of 547 nm) composed by two or more unit fibers with shorter diameter (average length of 128 nm) (Fig.5).
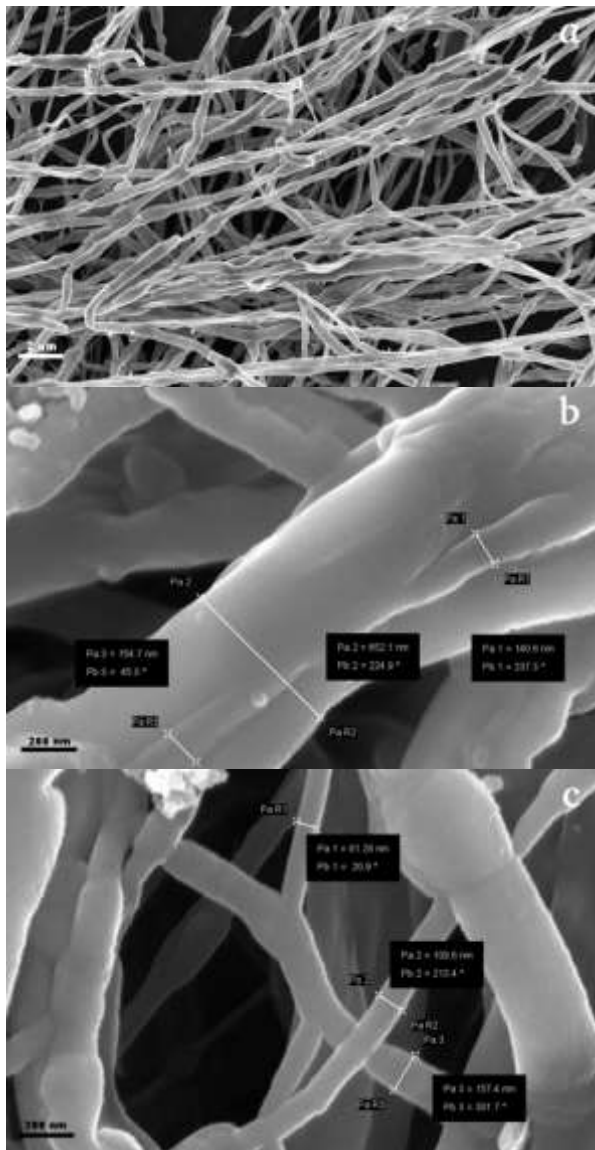
The same microscopy technique was applied to the PEO-VO$_2$ hybrid Nfs posteriorly produced, revealing that the morphology of the fibers was not modified by the presence of VO$_2$ NPs. The average diameter of the unit fibers is 128 nm and the formation of thicker fibers due the linear agglomeration of two or more unit fibers was also observed (Fig.6).
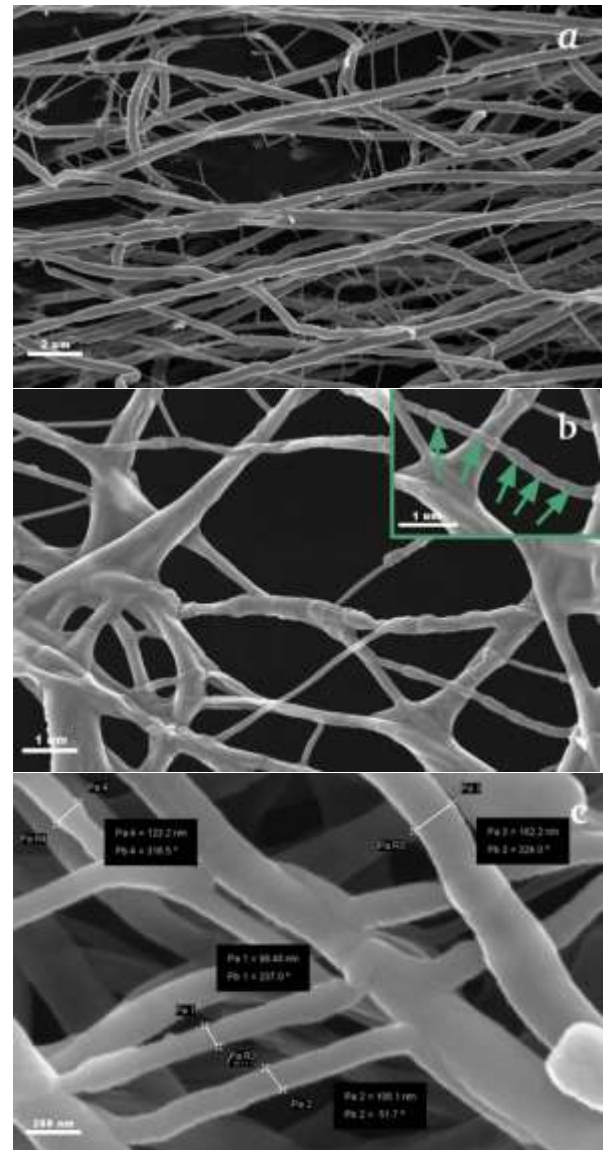

Figure 5. SEM images of pure PEO electrospun Nfs showing fibers general distribution within the sample (a); and typical transversal length for single and composed fibers (b, c).

Figure 6. SEM images of PEO-VO$_2$ hybrid electrospun Nfs, showing a) fibers general and typical distribution within the sample; b) fibers recurrent morphology that suggests a potential embeddement (green arrows in inset image) of the VO$_2$ NPs along the PEO fibers; and c) typical transversal length for single and composed Nfs.

Considering the average dimensions of the VO_2 NPs and based on the morphology presented by the fibers in some segments (Fig.6b), it could be hypothesised that the particles are embedded within the fibers, ordered in a longitudinal fashion along them. However, in order to ascertain the presence of the NPs within the fibers it was necessary to perform an elemental analysis by energy dispersive spectroscopy (EDS). This technique allowed us to identify what particular elements were present in the hybrid fibers as well as their relative proportion, demonstrating the high concentration of VO_2 in the fibers along with the expected components of PEO, i.e. carbon and oxygen, as well as small quantities of common contaminants such as calcium and sodium (Fig.7). Content of VO_2 NPs was also confirmed by TEM, demonstrating the presence of the characteristic atomic ordered array for metallic structures existing within the polymeric Nfs (Fig.8). TEM images allowed to identify symmetrical lattice fringes with interplanar distance calculated to be approximately 0.31 nm, wich corresponds to one of two alternating V-V bond distances of monoclinic VO_2 [27].
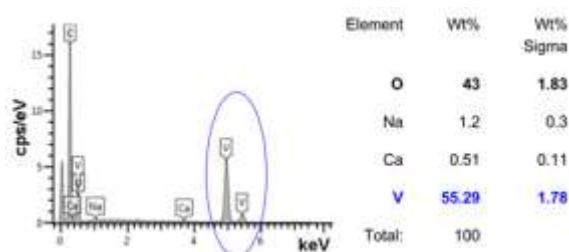

Figure 8. TEM image of PEO-VO_2 hybrid electrospun Nfs. It is possible to identify an aligned group of symmetrical lattice fringes (indicated by red arrows) with interplanar distance of 0.31 nm, which corresponds to one of two alternating V-V bond distances of the monoclinic phase of VO_2.

Backscattered electron images, obtained with the *Bruker EDS* equipment, displayed the compositional contrast that results from different atomic number elements and their distribution, evidencing the agglomeration of VO_2 NPs in specific points in the fibers (Fig.9). The presence of VO_2 NPs was not found uniformly distributed along the fibers, instead, the concentration of vanadium was detected only sparsely in some specific regions that formed accumulation of VO_2 NPs. In such closterisation regions it was possible to distinguish embedded shapes that correspond in dimensions to the NPs (Fig.9), confirming that the VO_2 NPs were entrapped in the fibers during electrospinning and tended to aggregate forming clusters within the fibers.

Element	Wt%	Wt% Sigma
O	43	1.83
Na	1.2	0.3
Ca	0.51	0.11
V	55.29	1.78
Total:	100	

Figure 7. EDS analysis of PEO-VO_2 hybrid electrospun Nfs. The table shows the relative concentration (Wt%) of elements present in the sample and their respective measurement errors (Wt% Sigma), demonstrating a high concentration of vanadium.
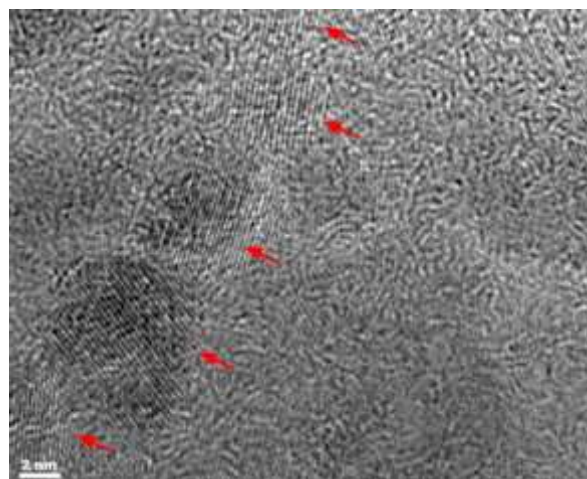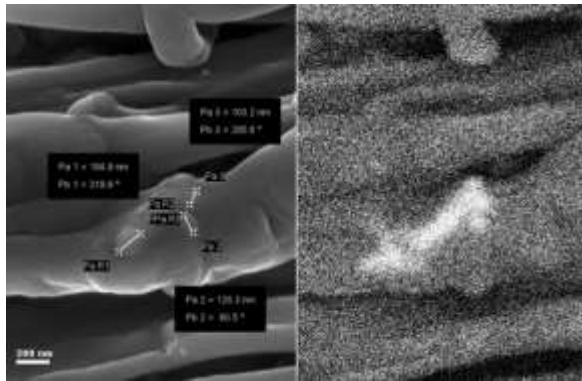
Figure 9. Back-scattered electron images produced by SEM of PEO-VO$_2$ hybrid electrospun Nfs. The highlighted area in the right image denotesthe presence of elements with higher atomic number, in this case VO$_2$, exhibiting agglomeration of the NPs within the fibers.
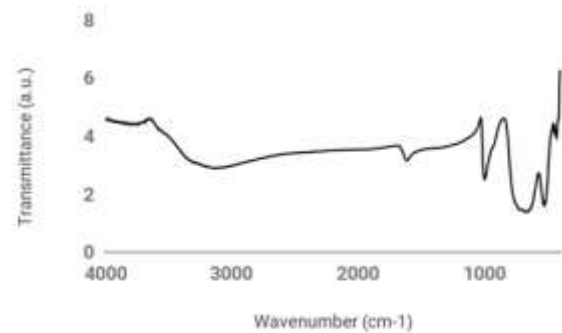

Figure 10. FTIR transmittance spectrum of VO$_2$ NPs, showing the characteristic vanadium dioxide strongest transmittance peaks at 422, 521 and 995 cm^{-1} and broad band centred at 680 cm^{-1}.

One possible reason for the agglomeration of the NPs is the low homogeneity of the polymeric solution achieved after incorporation of the NPs. Another hypothesis would be related to the influence of the electric field at the point of the electrospinning system emitter on the metallic NPs, which could have acted as a factor of accumulation of the NPs within the flux of the polymeric solution while passing through the emitter and during the formation of the Taylor cone.

FTIR characterisation

To further investigate the effect of the incorporation of VO$_2$ NPs during the synthesis of PEO fibers by electrospinning, the hybrid Nfs were analysed by FTIR spectroscopy. Firstly, a FTIR spectrum was obtained from the VO$_2$ NPs powder, displaying main vibrational bands at 422, 521 and 995 cm^{-1} (Fig.10), considered intrinsic to vanadium dioxide.

The bands at 422 and 521 cm^{-1} are attributed to V-O-V stretching vibrations, while the band at 995 cm^{-1} can be assigned to the coupled stretching vibration of the double bond V-O [28, 29]. A broad band centred at 680 cm^{-1} (with full width half maximum covering frequencies from 580-780 cm^{-1}) is also observed. This peak may be a convolution of previously reported peaks at 670 cm^{-1} [28] and 715 cm^{-1} [29], corresponding to the V=O coupled vibrations of VO$_2$ nanorods and sphere-like VO$_2$ NPs respectively. In figure 11 we show the FTIR spectra obtained from pure PEO Nfs (Fig.11a) and PEO-(VO$_2$ NPs) Nfs (Fig.11b), as well as both FTIR plotted together (Fig.11c) as an intensity visual comparison. In the first case, it was observed a typical vibrational spectrum of PEO (Fig.11a) with bands at 842, 1278, 1340 and 1348, 1465, 2887 cm^{-1}, attributed to CH$_2$ rocking, CH$_2$ twisting, CH$_2$ wagging double band, CH$_2$ scissoring and stretching of the C-H group vibrations respectively [30]. The peak at 1090 cm^{-1} corresponds to a C-O-C triplet, characteristic of semi-crystalline PEO, while the peak at 529 cm^{-1} belongs to the C-C-O bending region of PEO [30, 31]. The FTIR spectrum corresponding to the PEO-(VO$_2$ NPs) Nfs (Fig.11b) exhibits the clear dominance of the relative concentration of PEO with respect to VO$_2$, exhibiting a majority of bands belonging to PEO and only one vibrational band attributed to the

presence of VO$_2$ NPs at 740 cm^{-1}. This peak is associated to an upshifted V=O coupled vibration of VO$_2$ that can be correlated with changes in the V-O bond lengths [17] and is in good agreement with previously reported peaks at 768 and 756 cm^{-1} that result from the incorporation of PEO to different vanadium oxides [32]. The presence of the vibrational band at 740 cm^{-1} demonstrates a bonding interaction between the polymer and the metal oxide in the hybrid nanofibers.
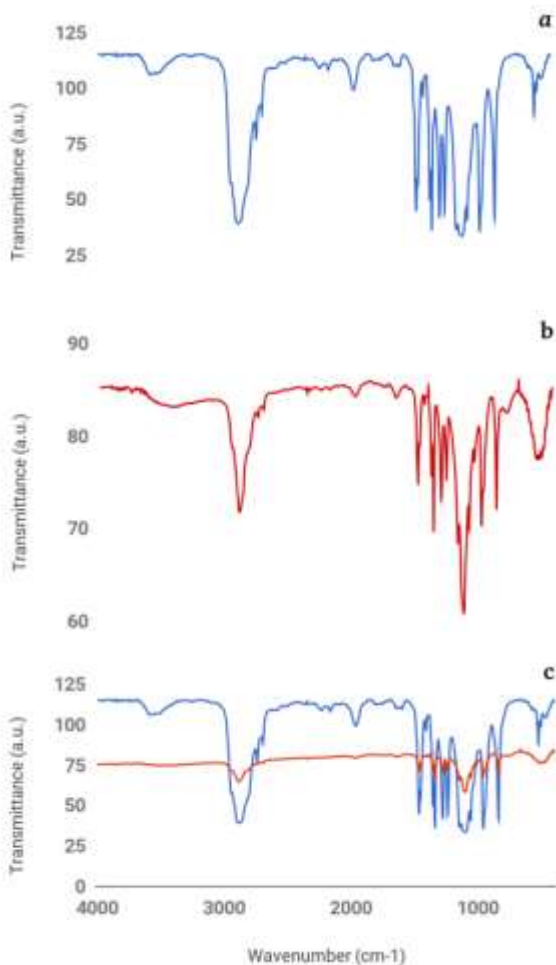

Figure 11. FTIR transmittance spectra a) PEO Nfs, showing a typical FTIR spectrum of PEO with main vibrational bands at 529, 842, 1090, 1278, 1340 and 1348, 1465 and 2887 cm^{-1}; b) PEO-(VO$_2$ NPs) Nfs, showing the same vibrational bands belonging to PEO with varied changes in peak intensity and a band at 740 cm^{-1} caused by presence of the VO$_2$ NPs; c) PEO Nfs (blue) and PEO-(VO2 NPs) Nfs (red) plotted together in order to illustrate the general reduction in peak intensity of the hybrid fibers compared to the PEO Nfs.

A general decrease in peak intensity with minimum band broadening is observed for all the spectrum bands (Fig. 11c). The decreased intensity of the spectrum peaks suggests a reduction of the change in dipole moment with respect to molecular bond distance of PEO [33] caused by the presence of VO$_2$ NPs (Eq. 1).

$$(\partial\mu/\partial x)_{PEO\ Nfs} > (\partial\mu/\partial x)_{PEO\text{-}VO2\ Nfs} \qquad \textbf{(Eq. 1)}$$

This general reduction in peak intensity can also be related to the change in relative concentration of PEO in the hybrid fibers, follwing the linear relationship between absorbance and concentration of the absorbing body [34]. Nevertheless, taking into account the low concentration of VO$_2$ in the hybrid fibers, in our case this effect could be considered close to negligible. Similar behaviour was observed in earlier reports of PEO-VO$_2$ hybrid nanomaterials [17, 35].

In terms of frequency shifts, the PEO-(VO$_2$ NPs) Nfs FTIR spectrum does not display significant changes or width alterations for the CH$_2$ vibrational bands, which suggests that no mayor modification of the polymer bonds strength, macromolecular conformations and crystalline structure takes place after addition of VO$_2$ NPs [17]. In particular, the conservation of the double wagging band at 1340 and 1348 cm^{-1} and the well resolved stretching band, with no significant width change, at 2877 cm^{-1} are both indicators of the semi-crystalline structure of the hybrid fibers [17, 32], in agreement with the results obtained from XRD.

The conservation of the C-O-C stretching triplet at 1090 cm^{-1} is further evidence of the semi-crystalline nature of the PEO-(VO$_2$ NPs) Nfs [30], also supporting that the presence of VO$_2$ NPs favours the crystallinity of PEO Nfs.

The most significant frequency shift is observed in the bending region of C-C-O, for the PEO spectrum band at 529 cm^{-1} that downshifts to 480 cm^{-1} in the PEO-(VO$_2$ NPs) spectrum, which indicates internal tension and changes in chain orientation [31, 36]. The reorganisation of PEO polar bonds due to the inclusion of VO$_2$ NPs modifies their average orientation, consequently affecting the maximum intensity of the FTIR spectrum peaks, as it is the case for the C-C-O band. A potential reduction of the number of deformations of the C-C-O bonds could also be associated with the change of intensity maximum and re-shape of this vibrational band [31].

The experimental evidence gathered in this work demonstrates the semi-crystalline nature of the PEO-(VO$_2$ NPs) Nfs. Based on these results, we suggest that the conservation of such structural characteristic could be favoured by the low dimensionality of our nanocomposite. This could be related to a potential decrease in entangled physical bonds formation in one-dimensional PEO composites compared to their bidimensional counterparts [36]. Moreover, the doping of PEO Nfs with VO$_2$ NPs has proved to enhance such crystalline nature of the hybrid fibers, characteristic that determines its properties and applications such as ion conductivity [37].

4. Conclusions

Organic-inorganic hybrid nanofibers were successfully produced by the electrospinning of a PEO solution containing VO$_2$ nanoparticles. It was demonstrated that it is possible to use the technique of electrospinning to fabricate PEO-(VO$_2$ NPs) nanofibers with high continuity and diameters between 100 and 600 nm, being the latter a longitudinal agglomeration of two or more nanofibers with average diameter of 128 nm. SEM images suggest that the VO$_2$ NPs are embedded within the nanofibers, possibly occurring during the process of electrospinning. Aggregation of the VO$_2$ NPs within the fibers was also evidenced by EDS. Following experiments will attain to maximise the homogeneity of this distribution. The results from XRD, showing two sharp peaks at 2Ө=19.35° and 23°, as well as the results from FTIR, displaying a C-O-C vibrational triple peak, a CH$_2$ double wagging band and a well resolved CH$_2$ stretching band, indicate that the PEO-(VO$_2$ NPs) nanofibers have a semi-crystalline structure.

PEO-VO$_2$ bidimensional nanocomposites tend to alter the semi-crystalline structure that PEO has in its natural state, modifying the molecular structure of the polymer and resulting in an amorphous material. We demonstrated that this novel uni-dimensional nanomaterial conserves the semi-crystalline structure of PEO, characteristic that determines better ionic conductivity. The presence of VO$_2$ adds electrochemical ionic storage capacity and thermochromic optical properties, constituting an enhanced nanomaterial with characteristics of particular interest for applications in optical data storage media, thermochromic functional coatings and in lithium and magnesium batteries for mobile devices and electric vehicles.

5. Acknowledgments

6. References

[1] Hu, Jiangtao, Teri Wang Odom, and Charles M. Lieber. "Chemistry and physics in one dimension: synthesis and properties of nanowires and nanotubes". *Accounts of chemical research* 32.5 (1999): 435-445.

[2] Wei, Qiulong, et al. "Porous One-Dimensional Nanomaterials: Design, Fabrication and Applications in Electrochemical Energy Storage." *Advanced Materials* 29.1602300 (2017): 1-39.

[3] Kuchibhatla, Satyanarayana VNT, et al. "One dimensional nanostructured materials." *Progress in materials science* 52.5 (2007): 699-913.

[4] Shi, Ye, et al. "Nanostructured conductive polymers for advanced energy storage". *Chemical Society Reviews* 44.19 (2015): 6684-6696.

[5] Knöller, Andrea, et al. "Strengthening of Ceramic-based Artificial Nacre via Synergistic Interactions of 1D Vanadium Pentoxide and 2D Graphene Oxide Building Blocks". *Scientific reports* 7 (2017): 40999.

[6] Duncan, Ruth. "The dawning era of polymer therapeutics". *Nature reviews Drug discovery* 2.5 (2003): 347-360.

[7] Huang, Zheng-Ming, et al. "A review on polymer nanofibers by electrospinning and their applications in nanocomposites". *Composites science and technology* 63.15 (2003): 2223-2253.

[8] Agarwal, Seema, Joachim H. Wendorff, and Andreas Greiner. "Use of electrospinning technique for biomedical applications". *Polymer* 49.26 (2008): 5603-5621.

[9] Taylor GI. Electrically driven jets. Proc R Soc London, Ser A 313 (1969):453–75.

[10] Fong H, Reneker DH. "Electrospinning and formation of nanofibers". *Structure formation in polymeric fibers* (2001): 225–246.

[11] Ahmed, Farah Ejaz, Boor Singh Lalia, and Raed Hashaikeh. "A review on electrospinning for membrane fabrication: challenges and applications". *Desalination* 356 (2015): 15-30.

[12] Hong, Gil Hwan, et al. "Highly permeable poly (ethylene oxide) with silver nanoparticles for facilitated olefin transport". *RSC Advances* 4.10 (2014): 4905-4908.

[13] Huang, Jiaxing. "Synthesis and applications of conducting polymer polyaniline nanofibers". *Pure and applied chemistry* 78.1 (2006): 15-27.

[14] Zhu, Rui, et al. "Fused silver nanowires with metal oxide nanoparticles and organic polymers for highly transparent conductors". *ACS nano* 5.12 (2011): 9877-9882.

[15] Zhang, Hua, et al. "A cost-effective method to fabricate VO_2 (M) nanoparticles and films with excellent thermochromic properties". *Journal of Alloys and Compounds* 636 (2015): 106-112.

[16] Jin, Ai Ping, Wen Chen, and Quan Yao Zhu. "Electrical and Electrochromic Characterization of Poly (ethylene Oxide)/Molybdenum Doped Vanadium Pentoxide Films". *Advanced Materials Research* 785 (2013): 771-774.

[17] Perera, Sanjaya D., et al. "Controlling interlayer interactions in vanadium pentoxide-poly (ethylene oxide) nanocomposites for enhanced magnesium-ion charge transport and storage". *Journal of Power Sources* 343 (2017): 580-591.

[18] Reddy, Ch V. Subba, et al. "Hydrothermal synthesis of hydrated vanadium oxide nanobelts using poly (ethylene oxide) as a template". *Journal of Power Sources* 179.2 (2008): 854-857.

[19] Glynn, Colm, et al. "Linking Precursor Alterations to Nanoscale Structure and Optical Transparency in Polymer Assisted Fast-Rate Dip-Coating of Vanadium Oxide Thin Films". *Scientific reports* 5 (2015): 11574.

[20] Arier, Ümit Özlem Akkaya, and Bengü Özuğur Uysal. "The electrochromic performances of single phase VO_2 nanoparticled films". *Surface and Coatings Technology* 302 (2016): 482-486.

[21] Takeuchi, Esther S., and Randolph A. Leising. "Lithium batteries for biomedical applications". *MRS bulletin* 27.08 (2002): 624-627.

[22] Deitzel, Joseph M., et al. "The effect of processing variables on the morphology of electrospun nanofibers and textiles". *Polymer* 42.1 (2001): 261-272.

[23] Ban, Chunmei. *Synthesis and characterization of nano-scale vanadium oxides, vanadium phosphates as cathodes for lithium batteries*. State University of New York at Binghamton, 2008.

[24] *Powder Diffraction Files*, Card No. 00-01901398, Database Edition, International Centre for Diffraction Data (ICDD), Newton Square, PA 19073-3273, USA 2005.

[25] Yang, Shuyan, et al. "Effect of molecular weight on conformational changes of PEO: an infrared spectroscopic analysis". *Journal of materials science* 50.4 (2015): 1544-1552.

[26] Jurado, J.F., Vargas Hernandez, and Vargas R.A. "Preparation of zinc oxide and poly-ethylene oxide composite membranes and their phase relationship". *Dyna* 79.174 (2012): 79-85.

[27] Rodriguez, Mark A., et al. "In-situ monitoring of vanadium dioxide formation using high-temperature XRD". *Powder Diffraction* 29.2 (2014): 97-101.

[28] Hou, Jiwei, et al. "Structural transition of VO_2 (A) nanorods studied by vibrational spectroscopies". *RSC Advances* 4.35 (2014): 18055-18060.

[29] Ji, Haining, et al. "Infrared thermochromic properties of monoclinic VO_2 nanopowders using a malic acid-assisted hydrothermal method for adaptive camouflage". *RSC Advances* 7.9 (2017): 5189-5194.

[30] Parveen, J. Shahitha, and SSM Abdul Majeed. "Poly (ethylene oxide)/Polyurethane based gel polymer electrolytes for lithium batteries". *International Journal of Scientific & Engineering Research* 4.12 (2013): 553-558.

[31] Bergeron, Carl, et al. "A study of the deformation, Network, and aging of polyethylene oxide films by infrared spectroscopy and calorimetric measurements". *International Journal of Spectroscopy* 2012 (2012):1-13.

[32] Mohan, V. M., Kenji Murakami, and Wen Chen. "The influence of PEO on the synthesis and electrochemical properties of VO_2 and V_3O_7 nH_2O nanobelts as a cathode for lithium battery". *Ionics* 18.6 (2012): 607-614.

[33] Smith, Brian C. *Infrared spectral interpretation: a systematic approach*. CRC press, USA, 1998.

[34] Mayerhöfer, Thomas G., Harald Mutschke, and Jürgen Popp. "Employing Theories Far beyond Their Limits—The Case of the (Boguer-) Beer–Lambert Law". *ChemPhysChem* 17.13 (2016): 1948-1955.

[35] Chen, Wen, et al. "Effect of modification by poly (ethylene oxide) on the reversibility of insertion/extraction of Li+ ion in V_2O_5 xerogel films". *Journal of Materials Chemistry* 12.6 (2002): 1926-1929.

[36] Yang, Shuyan, et al. "Effect of molecular weight on conformational changes of PEO: an infrared spectroscopic analysis". *Journal of materials science*50.4 (2015): 1544-1552.

[37] Stoeva, Zlatka, et al. "Ionic conductivity in the crystalline polymer electrolytes PEO_6: $LiXF_6$, X=P, As, Sb". *Journal of the American Chemical Society*125.15 (2003): 4619-4626.