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Polyethylene oxide assisted synthesis of titania fibers via electrospinning

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Advanced TiO_2 micro- and nano-fibers are synthesized combining electrospinning and sol-gel techniques. Original co-solvent approach is applied for preparation of spinnable solutions based on polyethylene oxide (PEO) and titanium isopropoxide (TIP). Two-steps thermal processing is developed for calcination of the as-spun composite fibers. Influence of PEO/TIP weight ratio on the fiber morphology is demonstrated via scanning electron microscopy. Based on X-ray and transmission electron diffraction analysis, opportunity for preparation of TiO_2 fibers consisting of anatase, brookite and oxygen deficient phases is demonstrated. The results obtained are encouraging for development of TiO_2 functional materials for application in photocatalysis and biomedical engineering.

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1. Introduction

Electrospinning technique is trying to take key positions in the development of micro- and nano-structured fibrous materials with high specific surface area, length-to-diameter ratios and porosity [1] The renewed interest to that relatively inexpensive, simple and exceptionally versatile technique could be primarily attributed to the synthesis of a broad set of low dimensional continuous fibers and possibilities for their alignment and spooling [2] Moreover, recently the electrospinning is successfully combined with chemical preparation techniques, thus remarkably expanding the wealth of engineered fibre materials over composites and ceramics. Generally, the method involves the application of a strong electrostatic field to a nozzle connected to a reservoir containing a spinning solution. Above certain threshold value of the applied electric field at which the repulsive electric force overcomes the surface tension a charged jet of the solution is ejected from the capillary tip. During the time of flight toward the collector the jet undergoes solvent evaporation and instabilities that decrease the fiber cross section down to nanometer range. Continues solid ultra fine, nano- and micrometer-sized fibers are collected on the surface of a counter electrode [3].

Titanium dioxide (TiO_2) is a binary compound that belongs to the family of refractive ceramics and environmental friendly materials having a large spectrum of applications in catalysis, solar cells production, sensorics, electronics, medicine etc. [4-8]

Two basic approaches could be distinguished for ceramic fibrous materials synthesis via electrospinning. The first one uses high molecular weight polymer that increases the viscosity of mixed solutions thus promoting their spinnability. In that way hybrid fibers are prepared. The preparation of pure ceramic fibers becomes possible after thermal processing under proper heating conditions. Following that approach hybrid poly(vinylpyrrolidone)/TiO_2 electrospun fibres from poly(vinylpyrrolidone)/titanium-tetra-iso-propoxide mixed solutions are successfully synthesized [9] Evolution of peaks of anatase TiO_2 phase is displayed on XRD spectra. Besides, varying a large number of parameters, such as the concentration ratio between poly(vinylpyrrolidone) and titanium-tetra-iso-propoxide [$Ti(OC_3H_7)_4$], strength of the electric field and feeding rate of the precursor solution, ceramic nanofibers having an average cross section diameter in the range 20 - 200 nm are obtained. Considering the great variety in the chemical composition and properties of the polymers and sol-gel solutions, these results seem very encouraging since they reveal a perspective toward synthesis of broad spectrum electrospun fibrous TiO_2 materials [2].

The second approach relates to a direct fabrication of pure ceramic fibers via electrospinning of viscous inorganic sols. In that case, however, complicated and time consuming procedures are necessary to control precisely either the solution viscosity that restrains sol-gel transition point [10-12] or the water content in the sol [13].

In our previous work the possibility to electrospun polyethylene oxide (PEO)/TiO_2 hybrid fibres from stable mixed solution of PEO and titanium-tetra-iso-propoxide (TIP) precursor in chloroform is demonstrated [14]. It is shown that the fibres obtained have a specific non-circular mesoscale cross section with clearly resolvable core and shell. This was attributed to the very fast evaporation of chloroform during jet time of flight. On the basis of X-ray diffraction analysis presence of anatase phase of titania in

the calcinated fibers was revealed. This stimulates our further experiments with typical for PEO and TIP solvents that possess lower vapour pressure as compared to that of chloroform. PEO was selected as a partner because it belongs to the family of nontoxic polymers that are biocompatible and therefore suitable for devices contacting with living organisms [15]. Besides, this inexpensive polymer is electrospinnable [16-18], it could assist a spinnability of mixed solutions [19] and finally could be removed efficiently from the hybrid fibers by thermal degradation [20].

The aim of the present work is to study the possibility for synthesis of titania micro- and nanofibers via electrospinning applying co-solvent approach during the preparation of polyethylene oxide/titanium-tetra-isopropoxide blend spinnable solutions. It is expected that the hybrid and ceramic fibrous mats thus prepared are suitable for broad spectrum of potential applications such as fibrous scaffolds for tissue and bone regeneration, photocatalysis etc.

2. Experimental

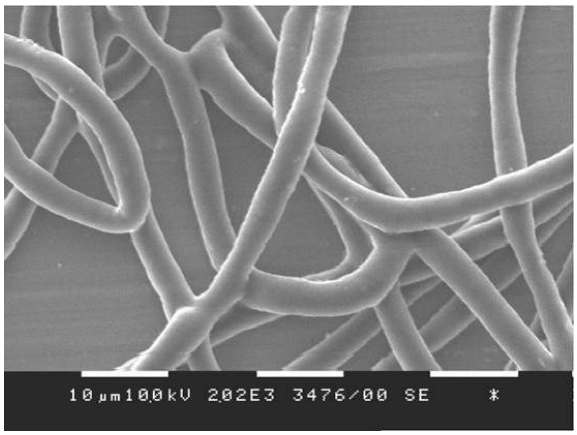
The average molecular weight - M_v, of polyethylene oxide (PEO "Badimol") was 800 000 as determined in distilled water at 30°C, using an Ubbelohde viscometer, by the equation: $\eta = 1{,}25.10^{-4}.Mv^{0.78}$ [20]. Titanium (IV) isopropoxide (TIP-"Fluka") was used as a precursor for the sol solution. Chloroform ($CHCl_3$) and ethanol (EtOH) were reagent grade ("Fluka") and were used without further purification.

In order to decrease the vapor pressure of $CHCl_3$ used previously as solvent [13] preliminary experiments were performed for preparing PEO spinning solutions with co-solvents of $CHCl_3$ and EtOH. It should be noted, that pure EtOH could not be used since it is practically inactive with respect to PEO dissolution [21]. In the present study it was established that homogeneous and stable PEO solutions can be prepared using co-solvent of EtOH and $CHCl_3$ up to an upper limit of 50/50 vol. %. That concentration was chosen for preparation of the starting 2 wt % PEO solution. Further, TIP was added dropwise to the latter and homogenized for 1 h via stirring. Thus, spinning solutions having PEO/TIP weight ratios of 20/1, 15/1, 10/1, 5/1 and 1/1were prepared. These solutions were immediately placed in a plastic syringe. A copper electrode, connected to a high-voltage power supply was immersed into the spinning solution. A grounded aluminum foil served as a counter electrode. High voltage between 15 and 30 kV was applied to the solution in the plastic syringe. The distance between the capillary tip and the counter electrode was 35 cm. In order to obtain pure ceramic fibers additional thermal processing was applied to the mats thus obtained. A part of the non-woven mats from all samples were further placed in a quartz tubular furnace and thermally modified via specially developed two-step calcination procedure [14]. The latter consisted in non-isothermal treatment of all samples for 2 hours at 360°C providing conditions of controlled PEO pyrolisis followed by further heating to 500°C and cooling down to room temperature. The mean heating rate of both thermal procedure steps was of the order of 10.0°C/min.

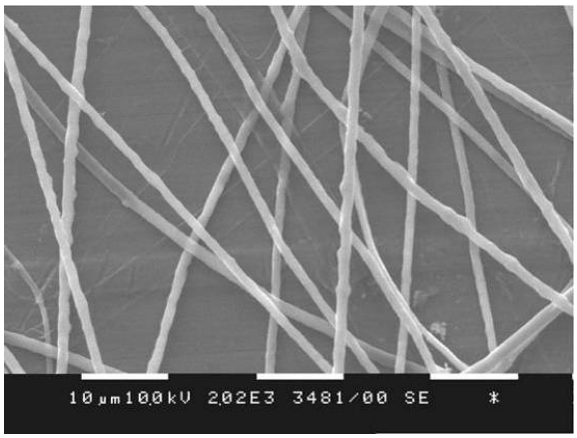
The morphology of the electrospun fibers was imaged under Philips 515 scanning electron microscope. The sample preparation technique consisted in consecutive deposition of nano-thick conductive carbon and gold films on the planetary rotating mats. Electron energy dispersive spectrometry (EDS) was applied in order to check the presence of Ti and its distribution along the as-spun hybrid fibers. The phase composition of the samples was studied using wide angle X-ray diffraction (WAXRD) analysis and in a special case via transmission high energy electron diffraction (THEED). The WAXRD spectra were recorded by means of Philips APD 15 spectrometer while the transmission electron imaging and corresponding selected area diffraction (SAED) patterns were performed under transmission electron microscope JEOL 200 CX.

3. Results and discussion

Fig. 1 presents the micro-morphology of pure PEO fibers electrospun from two different precursors based on 2 wt % PEO solution, the applied electric field (F_e) being 1 kV/cm. As seen from the scanning electron micrograph on Fig. 1a the PEO fibers that were prepared from 2% chloroform solution have an inherent diameter of several micrometers. Obviously, the easily volatile chloroform causes fast solidification of the jet and hinders its further stretching during the remaining time of flight to the collector. It should be noted here that the addition of TIP to that PEO solution results in an increase of the mean cross section of polymer/ceramic hybrid fibers [14]. As mentioned in the experimental part, it was established that PEO electrospinnable solutions can be successfully prepared using co-solvent of $CHCl_3$ and EtOH up to an upper limit of 50 /50 vol. %. The results from the morphological study of mats obtained, revealed a decrease of the mean fiber diameter with increasing the volume part of ethanol in that mixed solvent. Fig.1b demonstrate that the electrospun PEO fibers obtained from precursor based on co-solvent from 50/50 volt% ethanol and chloroform, results in fourfold decrease of mean fiber diameter. This was the reason for the choice of $CHCl_3$/EtOH 50/50 vol. % solution for the preparation of PEO starting precursors in further experiments on electrospinning of PEO/TIP solutions.

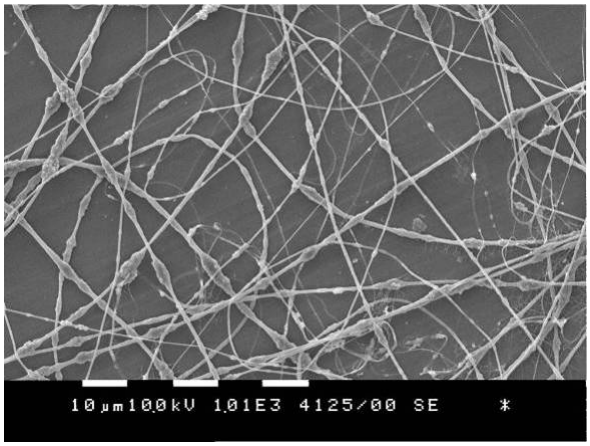


a

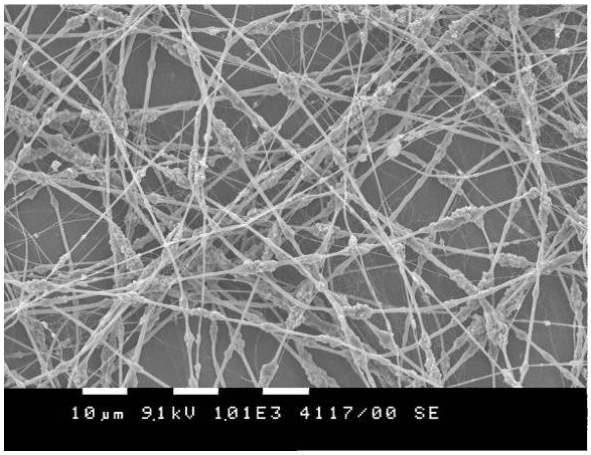


b

Fig 1. SEM micrographs of electrospun fibers obtained at applied field F_e=1 kV/cm from 2 wt% PEO solution and solvent: a - $CHCl_3$ and b - $CHCl_3$/EtOH in proportion 50/50 vol%. Magnification 2000.



a

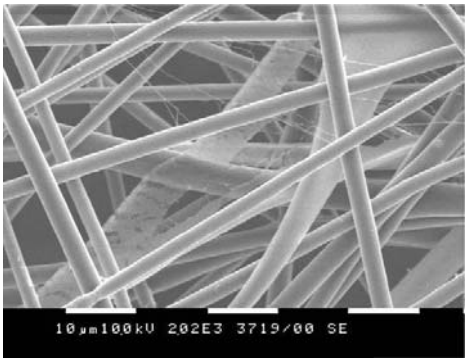


b

Fig. 2. SEM micrographs of as-spun hybrid fibers obtained at F_e=0.85 kV/cm, from different PEO/TIP solutions with weight ratio: 20/1(a) and 15/1 (b). Magnification 1000.

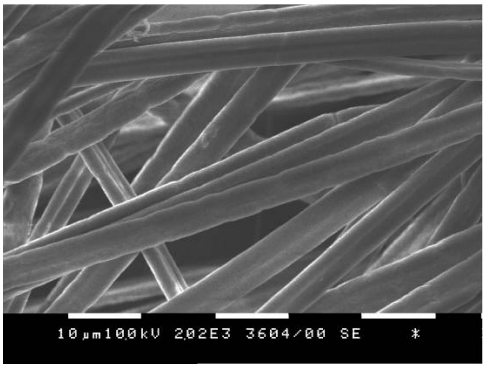
Following the experimental conditions established mixed solutions with PEO/TIP weight ratio in the range from 20/1 to 1/1 were prepared and further used for electrospinning experiments. Initially, it was found that the addition of TIP to PEO solutions is accompanied by a considerable increase of the electrospinning rate. Moreover, three-dimensional volumetric mats were obtained in the interval of PEO/TIP weight ratio between 10/1 and 1/1. At higher PEO concentrations (weight ratio between 15/1 and 20/1) fibers with bead defects, typical for low viscosity polymer electrospinning solutions [3], were obtained as demonstrated on Fig. 2. As seen, in that case, the mean fiber diameter in the defect free part is in the nanoscale range.

Substantially different is the morphology of as-spun mats prepared from PEO/TIP solutions with weight ratios 10/1 and 1/1, the applied field F_e being the same - 0.85 kV/cm (Fig. 3). Obviously, in both cases defect free micrometer sized cylindrical or ribbon like fibers were obtained. Similar fiber morphology was observed at PEO/TIP weight ratio 5/1. However, the percentage of the ribbon-like fibers was always lower than that of cylindrical and does not exceed 30%.



a

b



c

d

Fig. 3. SEM micrographs of hybrid fibers obtained at F_e=0.85 kV/cm, from PEO/TIP solutions with weight ratio 10/1 (a, b) and 1/1 (c, d) for as-spun (a, c) and calcinated,(b, d) fibres. Magnification 2000.

The comparison of the scanning electron micrographs on Fig. 3 c and 3 a unambiguously shows that the increase of TIP content in the spinning solution is accompanied by approximately two-fold increase of the mean cross section of the cylindrical fibres. This trend is more pronounced comparing the electrospun fibers on (Fig 3c and 3a) with those on Fig.1b. The origin of that great difference in the mean cross section dimensions between pure PEO and as spun hybrid fibers could be attributed to different mechanism occurring during the time of flight of the charged drop to the collector. These are correspondingly solvent evaporation or solvent evaporation combined with gelation, the latter prevailing during the formation of the hybrid fibers. Obviously, contribution of gelation is greater on increasing the TIP content in the spinning solution.

As mentioned in the experimental part, in order to obtain non woven mats of pure TiO_2 the as-spun fibers were thermally modified. The fibers prepared from PEO/TIP precursors with weight ratio in the range 10/1 - 1/1 were treated at high temperature by means of two stage calcination procedure [14]. The latter provided conditions for controlled PEO pyrolisis and efficient whipping off the emanating gases out of the heated quartz furnace, as well as for the occurrence of polycondensation and crystallization of the as-spun mats [20]. Applying that thermal processing to the samples studied measurable weight losses can be detected as evidenced by the data included on the Table 1.

Table 1.

PEO/TIP weight ratio	Initial sample weight, g	Final sample weight, g	Weight loss, %
10/1	0.0105	0.0057	45
1/1	0.0101	0.0075	25

Table Weight losses of electrospun fibrous samples with PEO/TIO weight ratio 10/1 and 1/1 after applying two-step calcination procedure for 2 hours at 360°C followed by further heating to 500°C and cooling down to room temperature. Mean heating rate ~ 4.0°C/min.

As seen from the Table, the higher is the polymer content the greater are the weight losses. Obviously, the latter are accompanied with a detectable decrease of mean cross section dimensions of as-spun hybrid fibers (Fig. 3a and 3c) as compared to the thermally modified fibers (Fig.3b or 3d respectively), their characteristic morphology being preserved. Therefore, the developed post-electrospinning heat treatment results in an efficient PEO pyrolisis of the hybrid fibers. The efficiency of the applied thermal processing is also supported by the observed preserving of the initial color of as-spun fibers in thermally processed fibrous samples.

Summarizing the results obtained it could be concluded that isotropic fiber contraction takes place under the thermal processing conditions used. However, due to the diversity of fibers morphology, as well as their random orientation, a statistical quantitative evaluation of

fiber mean cross section was difficult and even impossible. Roughly, the mean diameter of calcinated cylindrically-like fibers is within 1 - 3 μm size range, while the thickness of the ribbons is between 100 - 200 nm as seen from the high magnification images on Fig. 3b and 3d. The recorded Ti K_α X-ray map of as-spun composite fiber on Fig. 4 evidences a homogeneous Ti distribution in morphologically different fibers.

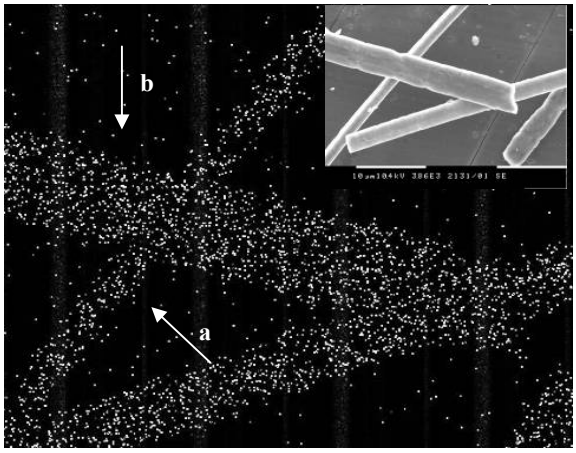


Fig. 4. SEM micrograph and corresponding Ti K_α X-ray map of as-spun PEO/TIP hybrid fibers for a – cylindrical and b – ribbon like fibers. The electrospinning parameters same as on Fig. 3c. Magnification 6500.

It should be noted here, that the oxygen content, as well as relative Ti/O concentration could be also obtained via X-ray microanalysis. However, this method cannot be applied for obtaining of information about the phase composition of the electrospun fibers. As known [22, 23] the different practical applications of TiO_2 based materials are strongly related to the type of titania polymorphs. For that purpose in the present work WAXRD-spectroscopy was applied for studying the crystallographic state of the calcinated fibers. The recorded X-ray diffraction spectra are shown on Fig. 5. PEO/TIP weight ratios, electrospinning parameters and thermal processing conditions correspond to those of the samples SEM imaged on Fig. 3. Detailed analysis of X-ray spectra of fibers electrospun from PEO/TIP precursor with 1/1 weight ratio reveals anatase polymorph of titania, as well as a strong peak at $2\theta = 26.66^o$ (d = 3.34 Å). The change of PEO/TIP weight ratio to 10/1 results in evolution of lower intensity peaks, that corresponds to brookite modification of TiO_2 [24]. In that case a strong peak also displays at $2\theta = 26.36^o$ (d = 3.38 Å). The intense peaks at 2θ of 26.66^o and 26.36^o could be attributed to oxygen deficient Ti-O compounds as Ti_8O_{15} and Ti_4O_7 [25, 26]. The XRD spectrum of samples electrospun from PEO/TIP precursor with 5/1 weight ratio is not presented on Fig.5. However, it reveals the presence of anatase and traces of oxygen deficient titanium oxide too. On this basis it could be concluded that a partial chemical reduction takes place during the calcination procedure leading to the evolution of Ti-O crystalline phases with lower oxygen content. This assumption is supported by analytical data that the PEO pyrolisis is accompanied by formation of intermediate products as acetaldehyde, formaldehyde and CO [20].

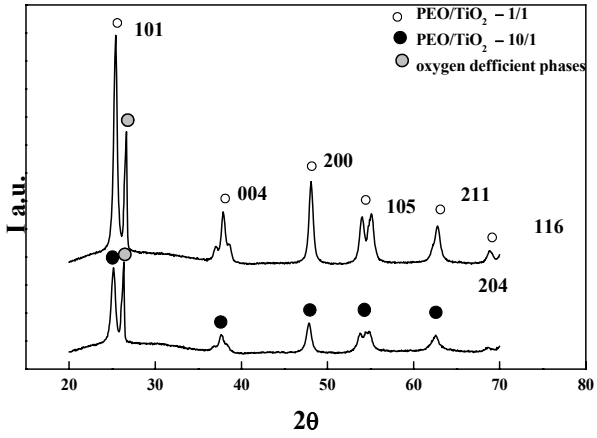
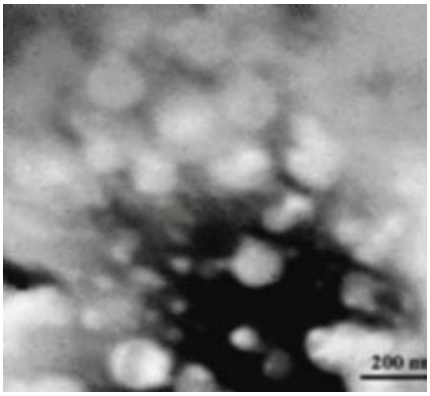


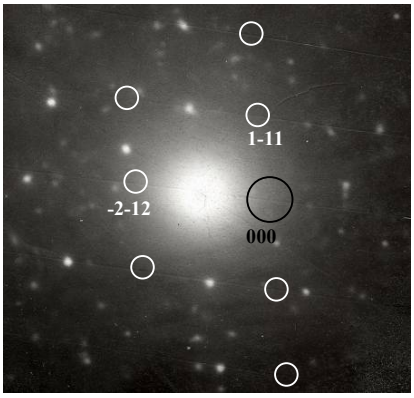
Fig. 5. Wide angle X-ray diffraction spectra of electrospun hybrid PEO/TiO_2 fibers with weight ratios 1/1 and 10/1 after consecutive calcination at 360 ^oC and 500 ^oC.

These compounds are well known reduction agents which have to provoke the TiO_2 reduction above 360°C during the two-step calcination procedure [19].

In addition, the opportunity of WAXRD spectra for semi-quantitative evaluation of the mean size of crystallites constituting the fibers of calcinated mats was also used in the present study. For that purpose Scherrer's relation was applied to the most intense recorded peaks of the spectra. Crystallites with mean size of 21 nm, 17 nm and 32 nm for (101) anatase, (210) brookite and those of oxygen deficient titanium oxide respectively, were estimated. Besides, we succeeded to obtain transmission electron images and corresponding SAED pattern, however for the thinnest ribbon like calcinated fiber, electrospun from solutions with PEO/TIP weight ratio 10/1. As seen from the high magnification dark field transmission electron image on Fig 6a crystalline aggregates built up of nano-sized entities and individual nano-sized crystallites could be distinguished in those fibers.



a.



b.

Fig. 6. High magnification dark field TEM micrograph of ribbon-like calcinated PEO/TiO_2 hybrid fiber - a, and b - the SAED pattern obtained from one of the visualized nano-crystals. The preparation conditions same as on Fig.3b. Magnification 85000 x.

As could be expected the electron diffraction analysis of individual nanocrystallites reveals the TiO_2 brookite structure. It is illustrated on Fig. 6b presenting the SAED pattern obtained from single TiO_2 nanoparticle in crystallographic orientation [143]: 82.59°

$$(1\bar{1}1)(\bar{2}\bar{1}2)(\bar{3}01)(\bar{1}\bar{2}3) \quad [24].$$
$$3.466 \quad 1.833 \quad 1.715 \quad 1.541$$

Obviously, the evolution of brookite is favored under specific preparation and calcination conditions.

Summarizing the results obtained, the present study demonstrate clearly that defect free nanostructured TiO_2 fibers could be prepared via electrospinning of PEO/TIP precursor combined with post-electrospun thermal calcination. Varying the PEO/TIP weight ratio in the range between 10/1 and 1/1, micrometer- or nano-sized fibers were obtained with mixed ribbon or cylinder-like morphology. Finally, a polycrystalline fiber structure was revealed, the identified crystalline modifications being anatase or brookite, as well as oxygen deficient Ti_xO_{2x-1} phase.

4. Conclusions

Stable mixed PEO/TIP solutions are prepared and electrospun in the range of weight ratios from 20/1 to 1/1 using chloroform and ethanol as co-solvent. It is established that PEO/TIP weight ratios of 20/1 and 15/1 favor the formation of hybrid fibers with bead defects. Further decrease of the weight ratio to 10/1 results in synthesis of defect free fibers with two distinctly different - ribbon-like and cylindrical, morphologies. The ribbons have an inherent thickness in the nanoscale range. Electrospinning of solutions with higher TIP content is accompanied by the evolution of fibers having round cross-section in the micrometer size range. It is found that after two stage calcination procedure the defect free fibers undergo detectable decrease of their mean size retaining their morphology. The results of X-ray and high energy electron diffraction analysis of calcinated fibers reveal co-existence of low oxygen deficient titania phases with brookite and anatase titania polymorphs.

The morphology and phase composition of synthesized TiO_2 fibers are challenges for further experimenting of their photocatalytic potential for air/water detoxification, as scaffolds for bone tissue engineering etc.

Acknowledgments

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