Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 3361–3365

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Fabrication of cadmium titanate nanofibers via electrospinning technique

Z. Imran [a,b,*], S.S. Batool [a,b], M.Q. Israr [a], J.R. Sadaf [a], M. Usman [b], H. Jamil [b], M.Y. Javed [c], M.A. Rafiq [b,*], M.M. Hasan [b], O. Nur [a], M. Willander [a]

[a] Department of Science and Technology, Campus Norrköping, Linköping University, SE-60174 Norrköping, Sweden

[b] Micro and Nano Devices Group, Department of Metallurgy and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences, PO Nilore, Islamabad 45650, Pakistan

[c] Laboratoire Matériaux et Phénomènes Quantiques, UMR 7162, Bâtiment Condorcet, Case 7021, Université Paris 7, 75205 Paris, Cedex 13, France

Received 9 November 2011; received in revised form 8 December 2011; accepted 17 December 2011

Available online 27 December 2011

Abstract

Here we present an electrospinning technique for the fabrication of cadmium titanate/polyvinyl-pyrrolidone composite nanofibers. The composite nanofibers are then annealed at 600 °C to obtain ilmenite rhombohedral phase cadmium titanate nanofibers. The structure, composition, thermal stability and optical properties of as synthesized and annealed cadmium titanate nanofibers are characterized by X-ray diffraction, energy dispersive X-ray spectroscopy, scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, Fourier transform infrared spectroscopy and ultraviolet–visible spectroscopy. The average diameter and length of the nanofibers are found to be ~150–200 nm and ~100 μm, respectively.

Keywords: A. Sintering; B. Fibers; B. Electron microscopy; Electrospinning

1. Introduction

Titanium based oxides are of great interest due to their high refractive index, direct wide energy bandgap and low absorption properties [1,2]. These oxides with pervoskite crystalline phase have diverse applications such as humidity sensors [3–5], gas sensors [6,7], microelectronic devices and photocatalytic cells [8,9]. One of these oxides, cadmium titanate ($CdTiO_3$) has an excellent dielectric, sensing and optical properties [10,11]. It crystallizes into ilmenite rhombohedral phase and pervoskite-type orthorhombic phase at annealing temperatures below and above 1000 °C respectively [12].

Nanofibers of titanium dioxide (TiO_2), silicon dioxide (SiO_2) and titanate oxides ($BaTiO_3$, $SrTiO_3$) have been prepared by electrospinning technique [13,14]. Until now, bulk $CdTiO_3$ and its thin films have been investigated widely [11,12,15], however, the synthesis of one-dimensional nanostructures of $CdTiO_3$ has been overlooked. The preparation of nanoscale structures holds various advantageous characteristics compared to the bulk material due to their smaller size resulting in a tremendous increase in the surface area to a volume ratio of the materials and can be extremely useful for numerous applications [16].

Electrospinning has become a highly fascinating technique for the synthesis of nanofibers due to its special ability for the fabrication of thin nanofibers with excellent homogeneity and high density. The procedure works in the presence of the externally applied high electric field among the spinneret containing initially prepared viscous solution and conducting plate. As the intensity of the electrostatic field increases it overcomes the surface tension of the solution, a jet starts to form nanofibers which have been elongated and collected on conducting plate. The uniformity, homogeneity and diameter of nanofibers are highly dependent on solution parameters (e.g. viscosity, conductivity, solvent solution, temperature, vapor pressure and precursors of the solution) as well as on the process parameters (e.g. shape of collector, geometry of spinneret, solution flow rate, a tip to collector distance, applied

* Corresponding authors at: Micro and Nano Devices Group, Department of Metallurgy and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences, PO Nilore, Islamabad 45650, Pakistan.
Tel.: +923455873434.
E-mail addresses: zahid.imran733@yahoo.com (Z. Imran), fac221@pieas.edu.pk (M.A. Rafiq).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.12.046

voltage) [17,18]. Here, we report the synthesis of ilmenite rhombohedral phase $CdTiO_3$ nanofibers with excellent homogeneity and purity using electrospinning technique. $CdTiO_3$ nanofibers have an average diameter ~150–200 nm and length ~100 μm. X-ray diffraction (XRD), energy dispersive spectroscopy (EDS) and Fourier transform infrared (FTIR) analysis confirm the purity and crystalline structure of nanofibers.

2. Materials and methods

Cadmium acetate $Cd(CH_3COO)_2{\cdot}2H_2O$ (Sigma Aldrich), acetic acid (CH_3COOH) (Sigma Aldrich), ethanol (C_2H_5OH) (Sigma Aldrich) and titanium tetra isopropoxide $Ti(CH_3)_2(CHO)_4$ (Sigma Aldrich) was used as precursors. Polyvinylpyrrolidone (PVP) (MW = 1,300,000) was used to control the

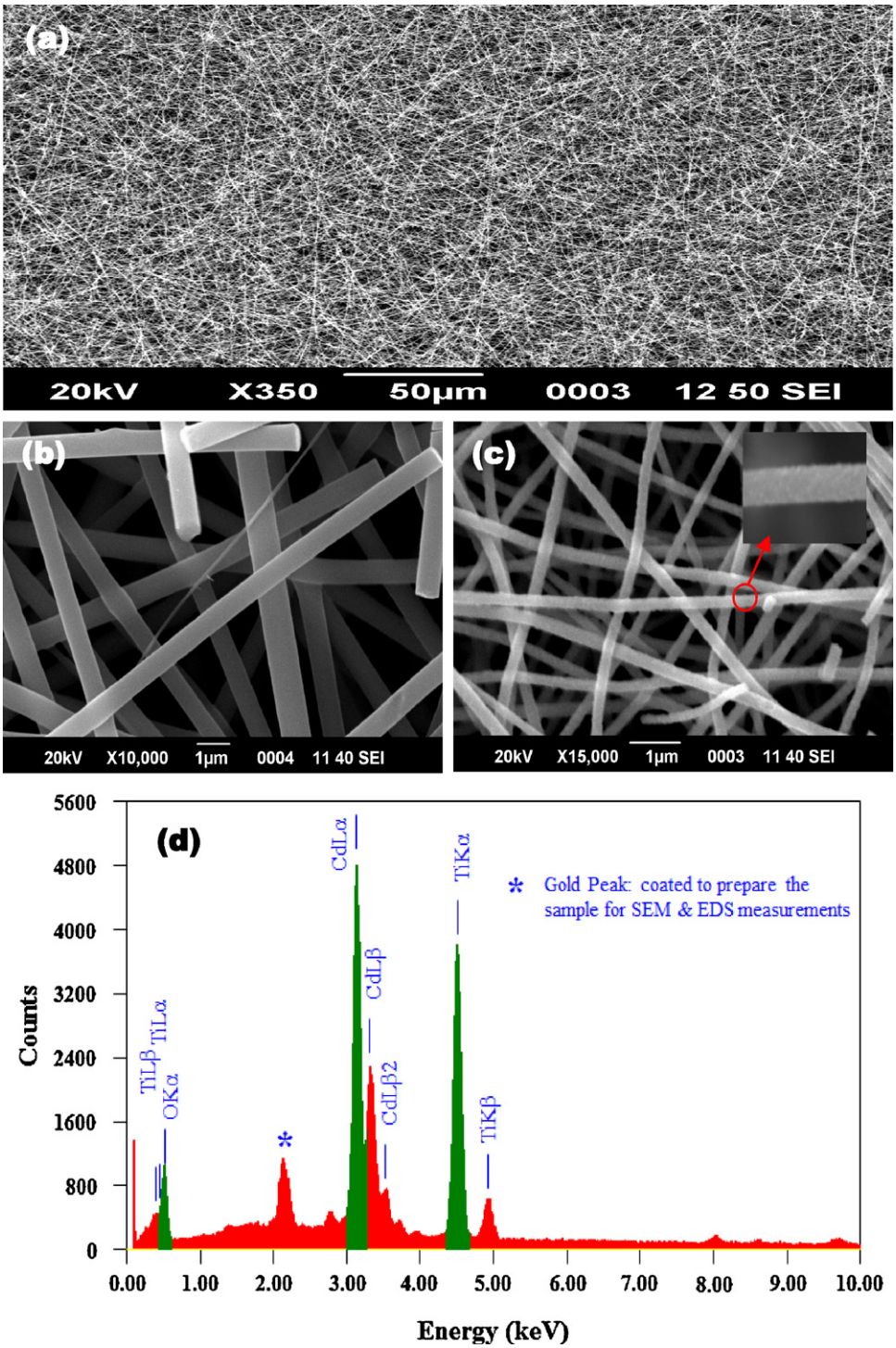

Fig. 1. Scanning electron micrograph of $CdTiO_3$ nanofibers (a) low magnification image annealed at 600 °C, (b) as synthesized $CdTiO_3$/PVP composite nanofibers, (c) high magnification annealed at 600 °C and (d) energy dispersive spectrum of nanofibers (EDS).

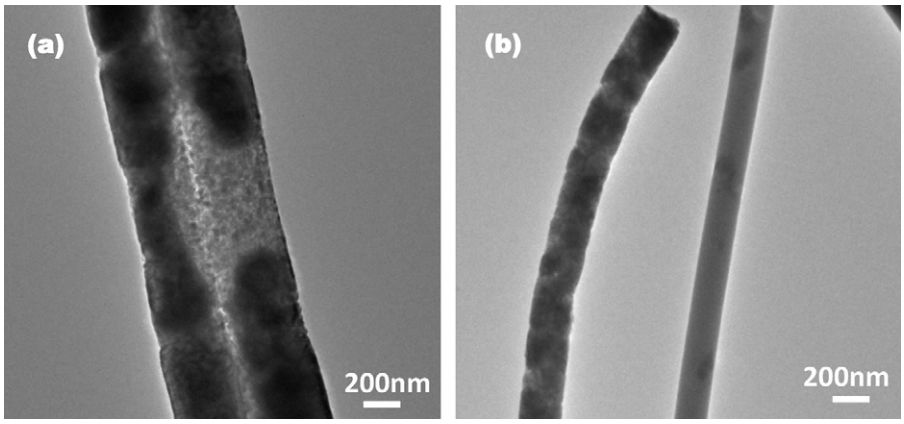

Fig. 2. TEM images (a) $CdTiO_3$/PVP nanofiber and (b) $CdTiO_3$ nanofibers annealed at 600 °C.

viscosity of the solution. The first solution of cadmium acetate was prepared by mixing 2 g of cadmium acetate in 4 mL of acetic acid at room temperature. The second solution was obtained by mixing an appropriate amount of PVP in ethanol by stirring for 1 h. Titanium tetraisopropoxide was then added drop wise in cadmium acetate solution with the molar ratio of 1:1. The solution was stirred for 2 h to obtain a homogeneous mixture. The solution was then loaded in a syringe with a 24-gauge needle. High electric filed ∼0.7 kV/cm was applied between the needle and the collector plate. The nanofibers were collected on aluminum foil placed on the collector plate. The as-spun nanofibers were dried in an oven at 80 °C for 3 h. PVP was then removed to obtain pure $CdTiO_3$ nanofibers by heating the dried nanofibers at 600 °C for 3 h with a heating rate of 5 °C/min.

X-ray diffraction (XRD) analysis was conducted on a Brag–Brentano X-ray diffractometer with $CuK\alpha_1$ radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) and transmission electron microscope images were obtained on a JSM-6490LA and Jeol 2010 (200 kV) Japan, respectively. Thermogravimetric analysis and Fourier transformation infrared (FTIR) spectroscopy was performed on a Q500 and Thermo Nicolet 6700 spectrometer, respectively. Ultraviolet–visible (UV–vis) absorption spectroscopy was performed using Perkin-Elmer Lambda 900.

3. Results and discussion

The SEM images of electrospun cadmium titanate nanofibers at 7 cm distance between syringe needle tip and collector are shown in Fig. 1. The surface morphology and size of the samples varied strongly depending on the annealing temperature. Fig. 1a shows the lengths of the annealed fibers are in the range of ∼100–200 μm. The surface of as spun $CdTiO_3$/PVP composite nanofibers dried at 80 °C in the oven is smooth due to the amorphous nature of $CdTiO_3$/PVP composite. Diameters of at least 15 fibers were measured for both as synthesized and annealed fibers. The range of the diameter of as synthesized composite nanofibers are in between ∼500 and 800 nm as shown in Fig. 1b and after annealing at 600 °C for 3 h, the PVP is fully decomposed, and a polycrystalline fiber is obtained (Fig. 1c). Due to PVP burn the diameters of the nanofibers are reduced to ∼150–200 nm shown in Fig. 1c, but their continuous microstructure is maintained. Due to PVP burn out ∼70% reduction of average diameter is observed. The inset in Fig. 1c at high resolution shows that the fibers are made up of grains. Fig. 1d shows the energy dispersive spectrum (EDS) of $CdTiO_3$ nanofibers which shows that the $CdTiO_3$ nanofibers hold good purity after removal of PVP.

Transmission electron microscopy (TEM) images of $CdTiO_3$/PVP nanofibers of as synthesized and annealed at 600 °C are shown in Fig. 2a and b respectively. The bright field TEM images show that the fibers consist of grains with the size of approximately 20–30 nm. The fabricated nanofibers are polycrystalline in nature; however, single crystalline nanofibers could be achieved through a post-annealing procedure beyond 1000 °C [19,20].

Fig. 3 shows the X-ray diffraction pattern of $CdTiO_3$/PVP composite nanofibers dried at 80 °C for 1 h in an oven and annealed at 600 °C. The dried sample indicates an amorphous state of nanofibers. After annealing at 600 °C for 3 h the polycrystalline structure of ilmenite rhombohedral phase and strong peaks are observed at $2\theta = 31.22°$ and $2\theta = 34.11°$ which

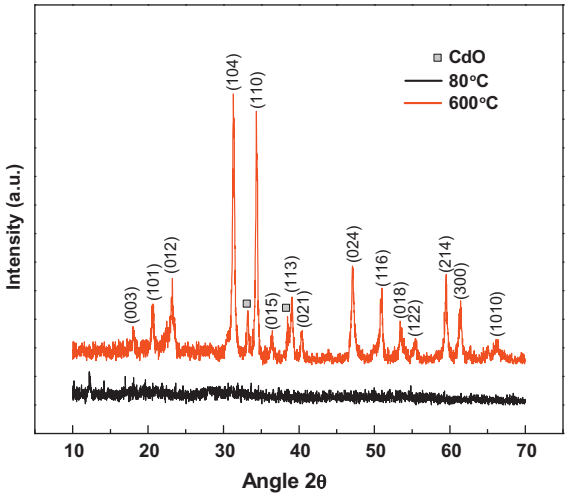

Fig. 3. X-ray diffraction pattern of $CdTiO_3$ electrospun nanofibers dried at 80 °C and annealed at 600 °C.

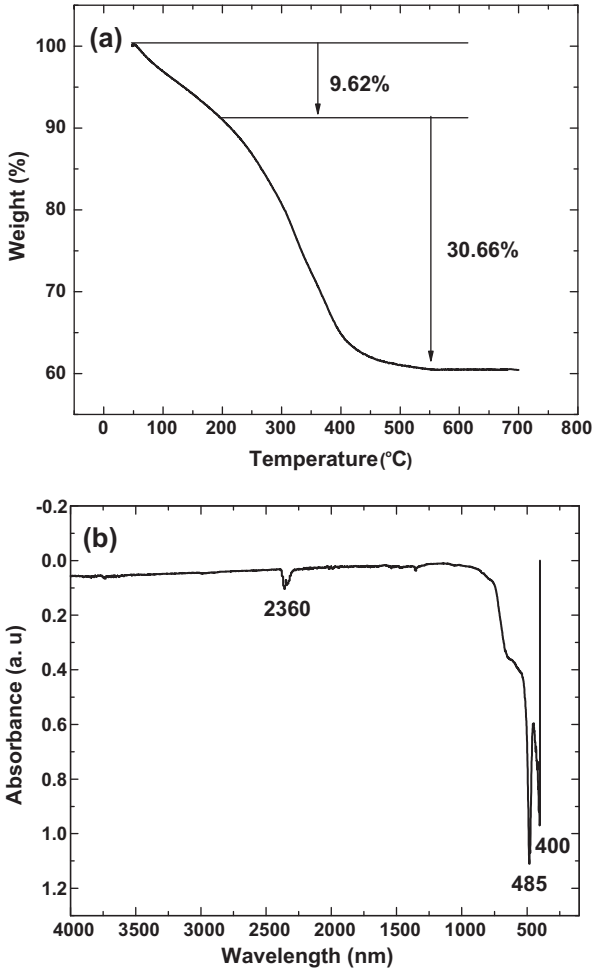

Fig. 4. (a) TGA curve of $CdTiO_3$/PVP nanofibers and (b) Fourier transform infrared spectrum of $CdTiO_3$ nanofibers heat treated at 600 °C.

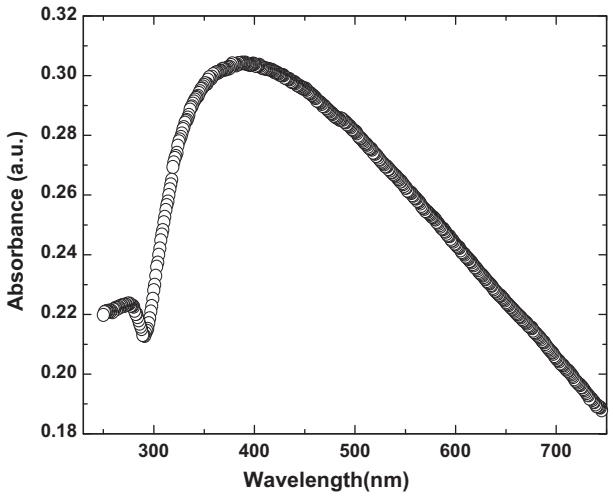

Fig. 5. Room temperature UV–vis absorption spectrum of $CdTiO_3$ nanofibers.

can be associated with (1 0 4) and (1 1 0) planes, respectively. No diffraction peaks corresponding to organic compounds are observed, implying that the PVP has been removed after the heat treatment at 600 °C. All diffraction peaks show good consistency with JCPDS, Card No. 29-0277 of ilmenite rhombohedral phase of $CdTiO_3$ [12]. However, a low-intensity peak at $2\theta = 33^\circ$ and 39° is found, which can be associated to the CdO (JCPDS Card No. 05-0640) and can be removed by further heating the sample at higher temperature [21]. The lattice parameters determined for the ilmenite rhombohedral phase are: $a = 5.29$ Å and $c = 14.874$ Å.

Fig. 4a shows the TGA curve of $CdTiO_3$/PVP composite nanofibers with a heating rate of 10 °C/min in nitrogen atmosphere. The weight loss started slowly from 50 °C, and the first step completed at about 200 °C. The weight loss in this region is about 9.62% which corresponds to the removal of moisture absorbed by the sample during the fabrication process as the polymers exhibit a high water absorption capacity [22–25]; in addition, the evolution of acetic acid remains in the nanofibers, derived from the starting acetate. A further weight loss of 30.66% was observed up to 530 °C which occur due to the evaporation of organic contents (PVP) [26,27]. No weight loss has been observed beyond the temperature value of 600 °C as the TG curve becomes horizontal. The TG curve confirms the formation temperature of the sample to be around 600 °C.

Fig. 4b shows absorption vs wavelength plot of the nanofibers using the FTIR spectroscopy. The absorption bands appearing at position of ~400 cm^{-1} and ~485 cm^{-1} are associated with Cd–O bands [12]. Absorption bands related to PVP are absent, which lead us to the conclusion that the annealing of $CdTiO_3$/PVP composite nanofibers at 600 °C results in complete removal of PVP from the nanofibers. The band observed at ~2360 cm^{-1} has been attributed to the CO_2 absorbed on the surface of the nanofibers from the atmosphere [28].

Fig. 5 depicts the UV–vis absorption spectrum of $CdTiO_3$ nanofibers measured in the range of 200–800 nm. The spectrum has been recorded using a homogeneously suspended solution of nanofibers in isopropanol with the molar ratio of 1:100. The spectrum shows a broad absorption peak with the centered at around 380 nm along with an absorption tail at the lower energy (250 nm) which could be attributed to the electron–hole recombination in CdO, which is present in the $CdTiO_3$ nanofibers according to XRD results.

4. Conclusions

Here, we report the fabrication of $CdTiO_3$ nanofibers having an average diameter of ~150–200 nm and length of ~100 μm using electrospinning technique. Scanning electron microscopy results reveals the porous surface of the nanofibers while the compositional purity and crystalline structure with the ilmenite rhombohedral phase of nanofibers has been observed from EDS, XRD and FTIR analyses. Combining the XRD and TEM results, it could be concluded that nanofibers contains polycrystalline structure and grains with different sizes. Additionally, the absorption peak at a wavelength of 380 nm could be related to the wide-band gap of the nanofibers. Therefore, we believe that the fabricated $CdTiO_3$ could hold an excellent potential for UV photonics and sensing applications.

Acknowledgement

The authors acknowledge the financial support from Higher Education Commission, Pakistan.

References

[1] S. Pavasupree, N. Laosiripojana, S. Chuangchote, T. Sagawa, Fabrication and utilization of titania nanofibers from natural leucoxene mineral in photovoltaic applications, Jpn. J. Appl. Phys. 50 (2011) 1–4.
[2] J. Watthanaarun, V. Pavarajarn, P. Supaphol, Titanium (IV) oxide nanofibers by combined sol–gel and electrospinning techniques: preliminary report on effects of preparation conditions and secondary metal dopant, Sci. Technol. Adv. Mater. 6 (2005) 240–245.
[3] Y. Sadaoka, M. Matsuguchi, Y. Sakai, H. Aono, S. Nakayama, H. Kuroshima, Humidity sensors using KH_2PO_4-doped porous (Pb, La)(Zr, Ti)O_3, J. Mater. Sci. 22 (1987) 3685–3692.
[4] R.E. Newnham, G.R. Ruschau, Smart Electroceramics, J. Am. Ceram. Soc. 74 (1991) 463–480.
[5] W.P. Tai, J.H. Oh, Fabrication and humidity sensing properties of nanostructured TiO_2–SnO_2 thin films, Sens. Actuators B: Chem. 85 (2002) 154–157.
[6] B. Ding, M.R. Wang, J.Y. Yu, G. Sun, Gas sensors based on electrospun nanofibers, Sensors 9 (2009) 1609–1624.
[7] S. Tsunekawa, T. Fukuda, A. Kasuya, Blue shift in ultraviolet absorption spectra of monodisperse CeO_{2-x} nanoparticles, J. Appl. Phys. 87 (2000) 1318–1321.
[8] X. Ma, T. Zhu, H. Xu, G. Li, J. Zheng, A. Liu, J. Zhang, H. Du, Rapid response behavior, at room temperature, of a nanofiber-structured TiO_2 sensor to selected simulant chemical-warfare agents, Anal. Bioanal. Chem. 390 (2008) 1133–1137.
[9] G. Laera, B. Jin, H. Zhu, A. Lopez, Photocatalytic activity of TiO_2 nanofibers in simulated and real municipal effluents, Catal. Today 161 (2011) 147–152.
[10] S.A. Mayen-Hernandez, J. Santos-Cruz, G. Torres-Delgado, R. Castanedo-Perez, J. Marquez-Marin, J.G. Mendoza-Alvarez, O. Zelaya-Angel, $CdTiO_3$ thin films prepared by sol–gel method using a simpler route, Surf. Coat. Technol. 200 (2006) 3567–3572.
[11] H. Wang, X.X. Zhang, A.P. Huang, H.Y. Xu, M.K. Zhu, B. Wang, H. Yan, M. Yoshimura, A new phase of cadmium titanate by hydrothermal method, J. Cryst. Growth 246 (2002) 150–154.
[12] M.R. Mohammadi, D.J. Fray, Low-temperature perovskite-type cadmium titanate thin films derived from a simple particulate sol–gel process, Acta Mater. 57 (2009) 1049–1059.
[13] J. Yuh, J.C. Nino, W.A. Sigmund, Synthesis of barium titanate ($BaTiO_3$) nanofibers via electrospinning, Mater. Lett. 59 (2005) 3645–3647.
[14] Y. Jing, S. Jin, Y.Z. Jia, J.D. Han, J.H. Sun, Preparation of $SrTiO_3$ nanofibers by hydrothermal method, J. Mater. Sci. 40 (2005) 6315–6317.
[15] A. Montenero, M. Canali, G. Gnappi, D. Bersani, P.P. Lottici, P. Nunziante, E. Traversa, Structural and electrical properties of sol–gel-processed $CdTiO_3$ powders and films, Appl. Organomet. Chem. 11 (1997) 137–146.
[16] J. Miao, M. Miyauchi, T.J. Simmons, J.S. Dordick, R.J. Linhardt, Electrospinning of nanomaterials and applications in electronic components and devices, J. Nanosci. Nanotechnol. 10 (2010) 5507–5519.
[17] N. Bhardwaj, S.C. Kundu, Electrospinning: a fascinating fiber fabrication technique, Biotechnol. Adv. 28 (2010) 325–347.
[18] T.J. Sill, H.A. von Recum, Electro spinning: applications in drug delivery and tissue engineering, Biomaterials 29 (2008) 1989–2006.
[19] P.C. Yu, R.J. Yang, Y.Y. Tsai, W. Sigmund, F.S. Yen, Growth mechanism of single-crystal alpha-Al_2O_3 nanofibers fabricated by electrospinning techniques, J. Eur. Ceram. Soc. 31 (2011) 723–731.
[20] J. Yuh, L. Perez, W.M. Sigmund, J.C. Nino, Electrospinning of complex oxide nanofibers, Phys. E: Low Dimen. Syst. Nanostruct. 37 (2007) 254–259.
[21] D. Bersani, P.P. Lottici, M. Canali, A. Montenero, G. Gnappi, Sol–gel preparation and Raman characterization of $CdTiO_3$, J. Sol–Gel Sci. Technol. 8 (1997) 337–342.
[22] S. Maensiri, M. Sangmanee, A. Wiengmoon, Magnesium ferrite ($MgFe_2O_4$) nanostructures fabricated by electrospinning, Nano. Res. Lett. 4 (2009) 221–228.
[23] U. Jianfeng, U. Donghui, I. Yujun, Fabrication and photocatalytic activity of ZnO–TiO_2 Nanofibers, Adv. Mater. 295–297 (2011) 1978–1981.
[24] J.S. Lee, Y.I. Lee, H. Song, D.H. Jang, Y.H. Choa, Synthesis and characterization of TiO_2 nanowires with controlled porosity and microstructure using electrospinning method, Curr. Appl. Phys. 11 (2011) 210–214.
[25] S.J. Park, G.G. Chase, K.U. Jeong, H.Y. Kim, Mechanical properties of titania nanofiber mats fabricated by electrospinning of sol–gel precursor, J. Sol–Gel Sci. Technol. 54 (2010) 188–194.
[26] X.W. Zhang, S.Y. Xu, G.R. Han, Fabrication, photocatalytic activity of TiO_2 nanofiber membrane, Mater. Lett. 63 (2009) 1761–1763.
[27] W. Sigmund, J. Yuh, H. Park, V. Maneeratana, G. Pyrgiotakis, A. Daga, J. Taylor, J.C. Nino, Processing and structure relationships in electrospinning of ceramic fiber systems, J. Am. Ceram. Soc. 89 (2006) 395–407.
[28] Y. Khan, S.K. Durrani, M. Mehmood, M.R. Khan, Mild hydrothermal synthesis of γ-MnO_2 nanostructures and their phase transformation to α-MnO_2 nanowires, J. Mater. Res. 26 (2011) 8.