Exp. Theo. NANOTECHNOLOGY 3 (2019) 269-280 https://doi.org/10.56053/3.3.269

Analysis and characterization of SiO_2 nanowires via electrospinning technique

T. Duńvki[*], *V. Saryviak*

Department of Materials Processing Technology, Silesian University of Technology, Konarskiego 18a Str., 44-100 Gliwice, Poland
*) Email: t.dunvki@polsl.pl

Received 20/12/2018, Accepted 25/4/2019, *Published* 15/9/2019

The aim of the study was the production of ceramic SiO_2 nanowires using the sol-gel and electrospinning methods from solution of PVP/TEOS/AcOH/EtOH. The obtained fibrous mats was subjected to preliminary drying at room temperature and next was subjected the calcination process in air to obtain pure amorphous silicon dioxide nanowires. Analysis of the morphology and chemical composition of the resulting nanowires was carried out using a scanning electron microscope (SEM) with energy dispersive spectrometer (EDS). In order to analyze the structure of the obtained materials were used high-resolution transmission electron microscope (TEM) and X-ray diffraction analysis (XRD). The analysis of the optical properties and the energy band gap of prepared nanowires was determined by spectral analysis of the absorbance in the function of the energy of radiation obtained using a UV-Vis spectrophotometer.

Keywords: Electrospinning; Nanowires; SiO_2; Optical.

Exp. Theo. NANOTECHNOLOGY 3 (2019) 269-280

1.INTRODUCTION

Over the past two decades, there has been a rapid development of nanotechnology in the field of oxygen nanomaterials, such as: nanoparticles [1,2] [3,4] nanofibers, nanowires [5- 7] or nanotubes [8-11] due to their unique features, impossible to achieve in the case of conventional materials. Simple oxides are of particular interest, both in terms of scientific research and possible wide applications, including aluminum (Al_2O_3), titanium (TiO_2), silicon (SiO_2), zinc (ZnO) and recently bismuth (Bi_2O_3). Considering the level of readiness of application of different oxides, special attention should be given to silicon oxide, commonly called silica, commonly occurring on the ground.

Nishikawa et al. observed that silica, at room temperature, as a result of excitation induced by an excimer laser with a power of 7.9 eV, is characterized with six photoluminescent bands in the energy range from 1.9 to 4.3 eV [12]. Radiation emitted by the amorphous wires SiO_2 corresponding to inter alia visible blue and green light allows to use this type of nanostructures as novel green-emitting phosphor [13] or full-colour display [14]. In addition, form-stable phase change materials made based on silica nanofibers, obtained using the sol-gel method and electrospinning, showed high efficiency of collection and storage of thermal energy [15. In addition, nanofibrous mats, SiO_2 and composite materials made of them are successfully used in the construction of innovative, flexible lithium-ion batteries [16] and water filters to adsorption of toxic cationic and anionic dyes, possible due to high porosity and specific surface of nano-structural silica [17].

So far, a number of nanowires and nanofibers SiO_2 manufacturing techniques have been developed. The most common include: physical vapour deposition, chemical vapour deposition, thermal decomposition, in which the growth of nanostructures is caused by vapour-liquid-solid (VLS) or solid-liquid-solid (SLS) mechanisms [18, 19]. These methods allow for full control of the morphology of the obtained nanomaterials, but manufacturing costs are too high, which makes it unprofitable to apply them to the manufacture of nanostructures on

Exp. Theo. NANOTECHNOLOGY 3 (2019) 269-280

an industrial scale. Increasing recognition is observed towards the method of manufacture of nanofibers SiO_2 connecting two techniques of manufacture, i.e. sol-gel and electrospinning of a polymer solution. Such techniques are relatively easy to connect, they do not require complicated operations and expensive equipment, and what is characteristic for this type of application, they are characterised by low manufacturing costs and the ability to use them on an industrial scale. In addition, when choosing the parameters of an electrospinning process and a spinning solution (e.g.: conductivity, viscosity and concentration of a precursor), and in the next stage of the manufacture of nanowires, the calcination process conditions, it is possible to obtain nanowires and nanotubes of silicon dioxide with a fully controlled and specific morphology [20].

The presented work describes the method to obtain a composite nanofiber on a polymer matrix, based and obtained from nanowires SiO_2 manufactured using the electrospinning and the sol-gel method. The analysis of the morphology, structure and chemical composition of the manufactured nanostructures of silica was carried out based on the microscopic tests (SEM, TEM) as well as analysis and x-ray micro-analysis (XRD, EDS). In addition, based on the spectroscopic tests (UV-Vis), the impact of the participation of the mass precursors in the spinning solution and the conditions of calcination of nanowires on optical features of the obtained nanomaterials was specified.

2. MATERIAL AND METHODOLOGY

2.1 Materials

For the preparation of spinning solutions, the following were used: poly (vinylpyrrolidone) (PVP, purity 99%, Mw=1 300 000 g/mole), ethanol (EtOH, purity 99.8%), acetic acid (AcOH, purity 99.8 %) and tetraethyl orthosilicate (TEOS, purity 99 %). Ethyl alcohol was provided by Avantor Performance Materials Poland, the remaining reagents and polymer were purchased from Sigma-Aldrich.

2.2 Methodology

Exp. Theo. NANOTECHNOLOGY 3 (2019) 269-280

In the first stage of the preparation of spinning solutions, the same two 10% (weight) mixtures of polymer in ethanol were prepared by adding 2 g of PVP to 22.8 ml EtOH, which then was stirred in magnetic stirrers for 60 min. In the next stage of the tests, a mixture of 1 ml of TEOS with 3 ml AcOH (first spinning solution) was added to the first polymer solution, while 4 ml of TEOS, and 3 ml AcOH (the second spinning solution) was added to the second solution, which was then stirred for 24 hours. Directly after mixing, the solution was placed in a device pump and electrospinned. Nanofibers were obtained using FLOW - Nanotechnology Solutions Electrospinner 2.2.0-500. During the electrospinning process, fixed parameters were applied, i.e.: distance and tension between a nozzle and a manifold (15 cm, 19 kV)) and a flow rate of a solution of 1.5 ml/h. In order to analyse the morphology and the structure of the manufactured materials, nanofibers were placed directly on copper mesh-shaped holders. In the case of UV-Vis and XRD analyses, specially prepared glass substrates were applied. Directly after a sample was manufactured, it was left to dry at room temperature, and then it was subjected to the calcination process in a tube kiln PRC75 by Czylok, at a temperature of 600°C, in atmospheric air for 2 h.

In order to analyze the morphology and the structures of the obtained materials, a high-resolution transmission electron microscope (TEM) TITAN 80-300 FEI was used for imaging in transmission mode as well as scanning-transmission mode, with the use of light and dark field (BF, DF), HAADF detector and filtration of energy, in particular using analytical electron microscopy in nanoareas in STEM mode and x-ray dyfractometer (XRD) X'Pert Pro by Panalytical. The measurement was carried out by the stepping method (a step every 0.026 ° and sometimes a step equal to 30s) in the geometry of Bragg-Brentano by using a detector PIXcel 3D on a bent axis beam. Filtered radiation of a lamp with a cobalt anode ($\lambda K\alpha = 0.17909$ nm) powered with 40 kV with current glow of 30 mA. In addition, to image the topography of the area and analyse the chemical composition of the manufactured nanomaterials, a scanning

electron microscope (SEM) Zeiss Supra 35 with x-ray spectrometer Trident XM4 series (EDX) were used.

Analysis of the optical properties of the obtained materials was carried out using a UV/VIS spectrophotometer Evolution 220 Thermo-Scientific. During the test, a light beam with a wavelength in the range of 190-1100 nm was on a sample at an angle of 8°. The method presented in works [21, 22] was applied to specify energy breaks.

3. RESULTS AND DISCUSSION

3.1 Analysis of structure, morphology and chemical composition

An analysis of the morphology and the structure of nanofibers prior to the calcination process showed that both fibres obtained from the first spinning solution containing 1 ml of TEOS (Figure. 1a) and the second one, with four times the amount of a precursor (Figure. 1 c) are without defects in a structure and have a constant diameter along the entire length. This fact testifies to the high viscosity of the manufactured solutions resulting from a uniform dispersion of precursor molecules between polymer [24] and relevant parameters of the electrospinning process that allowed to obtain output materials to ensure the manufacture of nanowires SiO_2 with specific morphology. A hundred-fold diameter measurement of random fibres obtained from the first spinning solution showed that the measured diameters ranged from 200 to 1000 nm, with the most common values for the diameter (30% of all measured values of diameters) contained in the range of 500 to 600 nm (Figures 1a – histogram). Similar results were recorded for nanofibers obtained from the spinning solution containing 4 ml of TEOS, i.e. the most common diameters were from the range from 500 to 600 nm, representing 29% of all fibres (Figure 1 c – histogram), except that the range of the measured diameter was wider and ranged from 100 to 1200 nm.

Exp. Theo. NANOTECHNOLOGY 3 (2019) 269-280

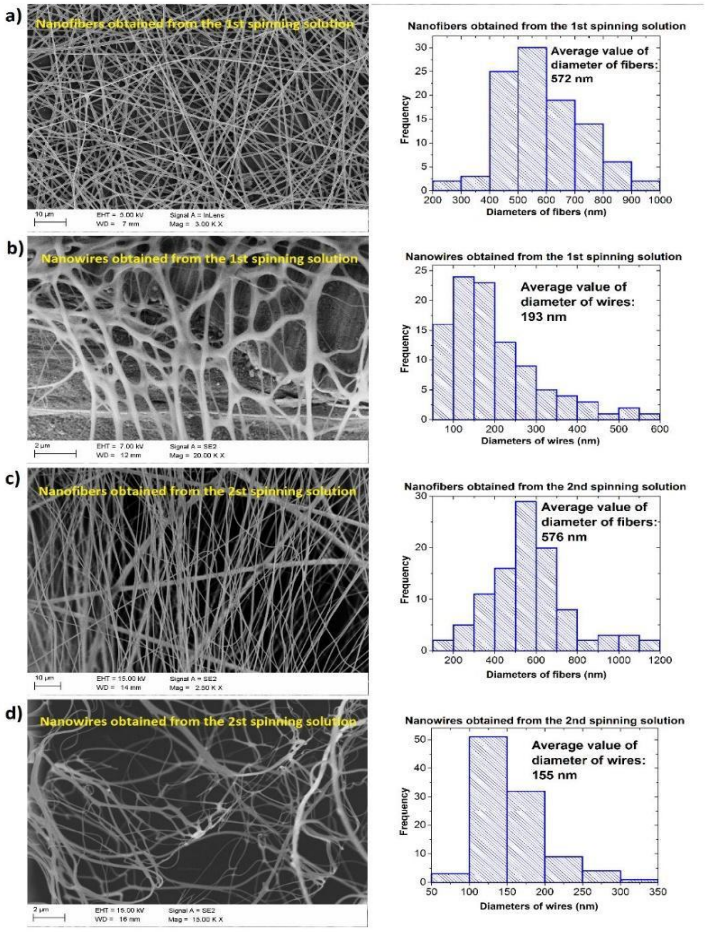

Figure 1 Surface morphology images of the produced composite nanofibers PVP/SiO2, nanowires SiO2 and histograms showing the distribution of the measured diameters of the tested nanomaterials: a), b) nanofibers and nanowires obtained the first spinning solution containing 1 ml of TEOS, c), d) nanofibers and nanowires obtained from the second spinning solution containing 4 ml.

Heating of the obtained fibrous composite mats PVP/SiO_2 at a temperature of 600°C for 2 hours contributed to the obtainment of pure SiO_2 nanowires with a much smaller diameter compared to the output nanofiber diameters, which coincides with the results shown in the work [24]. Measured diameters of nanowires of silicon dioxide, made from fibres derived from the first spinning solution contained in the range from 50 to 600 nm. The largest group included nanowires with diameters from 100 to 150 nm, which accounted for 23% of all the measured nanowires of the sample (Figure. 1b – histogram). Nanowires SiO_2 from nanofibers with four times the number of a precursor of THESEOS, compared to those obtained with the first spinning solution, characterised by lower variety of diameters. In addition, there

were no meshed as a result of sintering of nanowires together. For this sample, a hundredfold measurement of randomly selected nanowires showed that the measured diameters included in the ranges from 50 to 350 nm, and 50% of all nanowires was with diameters in the range from 100 to 150 nm. The carried-out analyses of the morphology of manufactured nanowires of silicon dioxide clearly testify to the significant impact of a number of a precursor of TEOS in the spinning solution on a size of a diameter of tested nanomaterials and their structure. The phenomenon of formation of defects in the structure in the form of places where nanowires sintered together (Figure. 1B) probably can be overcome by using lower calcination temperature, which results from the tests presented in the work [23].

In order to analyze the structure and chemical composition of the manufactured nanowires SiO_2, the tests were carried out using x-ray dyfractometer XRD and x-ray spectrometer EDX. On a dyfractometer registered for composite nanofibers PVP/SiO_2 made of a solution containing 4 ml of a precursor of silicon dioxide, and undergoing the calcination process at a temperature of 600°C for 2 hours, a wide/fuzzy line of diffraction, i.e. widening of liquid, was observed, resulting in the diffraction of the x-ray radiation beam obtained on the amorphous structure (Figure. 2a). The angular position of the diffraction line corresponded, in accordance with the data contained in the database JCPDS-ICDD, to the amorphous structure SiO_2. The obtained EDS spectrum from the areas shown in Figure. 1b, d, showed that for both nanofibers made of 10% polymer solution PVP in ethanol doped with a mixture of 1 ml of TEOS in 3 ml of acetic acid, and a solution containing four times more precursor of TEOS, a result of the calcination process, nanowires with a chemical composition and stoichiometry composition corresponding to a chemical solution of SiO_2 was obtained, as evidenced by the recorded peaks for oxygen and silicon (other peaks are derived from a substrate material, on which nanowires were embedded) (Figure. 2b, c).

Exp. Theo. NANOTECHNOLOGY 3 (2019) 269-280

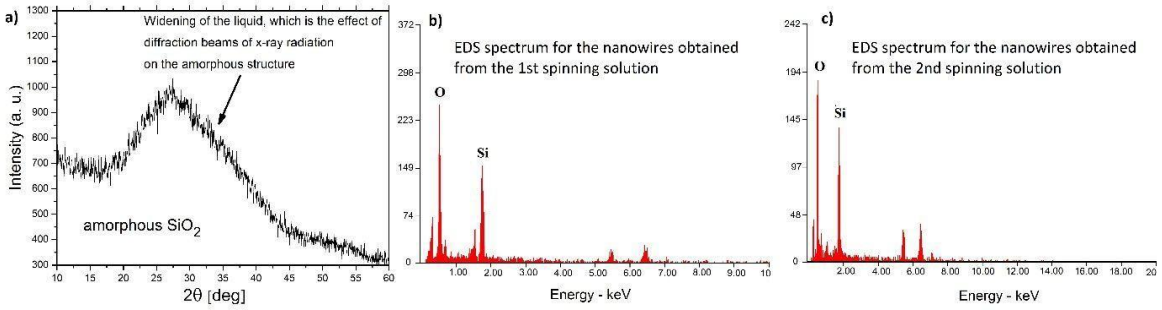

Figure 2 The analysis of the structure and the chemical composition of the obtained nanowires SiO2: a) XRD spectrum, b, c) EDS spectrum of nanowires manufactured sequentially from the first and the second spinning solution.

Figure. 3 shows the TEM images for the tested nanowires SiO_2 made in a transmission electron microscope in both modes of light and dark fields, and using HAADF detector. The diffraction test results, obtained using an analytical electron microscopy in nanoareas in STEM mode, confirmed the phase composition and the amorphous structure of the tested nanowires. Electron diffraction spectrum, obtained for a single nanowire SiO_2 (manufactured using the second spinning solution), in the form of diffraction reflections in the shape of fuzzy rings, resulting from electron beam scattering characteristic for the amorphous structure, proves their amorphous construction (Figure. 3c). The obtained TEM images (Figure. 3a, b) showed a consistent contrast throughout the tested nanowires of silicon oxide, which is indicative of the dense nature. The areas shown in Figure. 1a, b, where a stronger contrast of a place of imposition of individual nanowires SiO_2 on each other is visible. The analysis of the structure of a single nanowire, obtained from the second spinning solution (Figure. 3c), showed that it consists of interconnected, small crystallites SiO_2 of varying size and shape. In addition, the surface of the tested nanowire was even and pore-free.

Exp. Theo. NANOTECHNOLOGY 3 (2019) 269-280

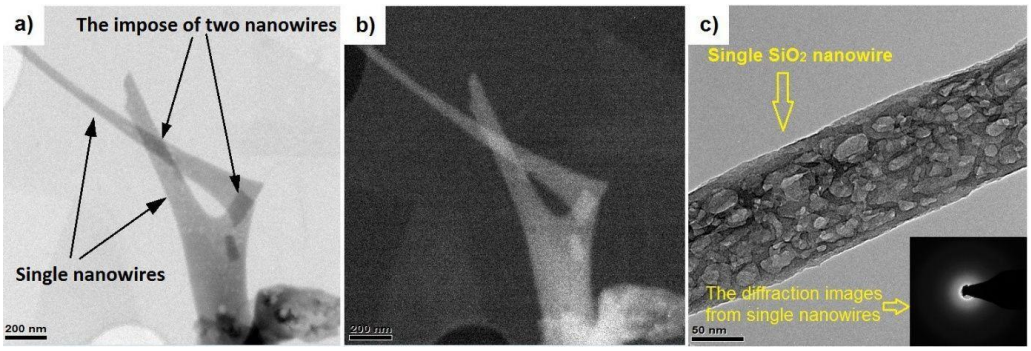

Figure 3 TEM images of the tested nanowires SiO2 (obtained from the second spinning solution): a) an image in a light area, b) an image in a dark area, c) a diffraction image from single nanowires obtained using analytical electron microscopy in nanoareas in STEM.

3.2 Analysis of optical properties

In order to determine the optical properties of the manufactured fibrous mat PVP/SiO_2 and amorphous nanowires SiO_2, an analysis of the spectrophotometry UV-Vis was carried out (figure. 4). Spectral characteristics recorded for nanofibers PVP/SiO_2 showed a significant impact of the participation of TEOS precursor on the optical properties of the obtained composite materials. UV-Vis spectrum for the fibrous layer obtained from the spinning solution containing 1 ml of a precursor of silicon dioxide has a sharp edge absorption for electromagnetic waves in close ultraviolet region below 330 nm, and maximum absorption was for a wavelength of 259 nm. For nanofibers presented in Figure. 1c, the obtained spectre was also characterised with a strong absorption in the ultraviolet range, the observed shift of absorption edge in the direction of greater energy, below 312 nm (Figure. 4a – before calcination). This is probably caused by four times greater participation of TEOS in the spinning solution, in relation to the nanofibers shown in Figure. 1a, obtained from the first solution. Spectral characteristics registered for nanowires manufactured both from the spinning solution containing 1 ml and 4 ml precursor overlap each other (Figure. 4a – after calcination in 600°C). In both cases of nanowires SiO_2, a strong increase in absorbance from approx. 2.5 to 3 was observed in relation to the spectra recorded for nanofibers prior to their high temperature, whereby absorption edges match the waves with a length of 325 nm. This fact testifies to a potential application of the manufactured nanostructures of silicon dioxide for

Exp. Theo. NANOTECHNOLOGY 3 (2019) 269-280

photocatalytic applications. The obtained results are similar to the results shown in the works [24], and the offset of absorption edges for SiO_2 towards greater energy is probably due to two times higher temperature during the calcination process of the manufactured composite mats PVP/SiO_2 compared to the temperature used by Nandanwar et al.

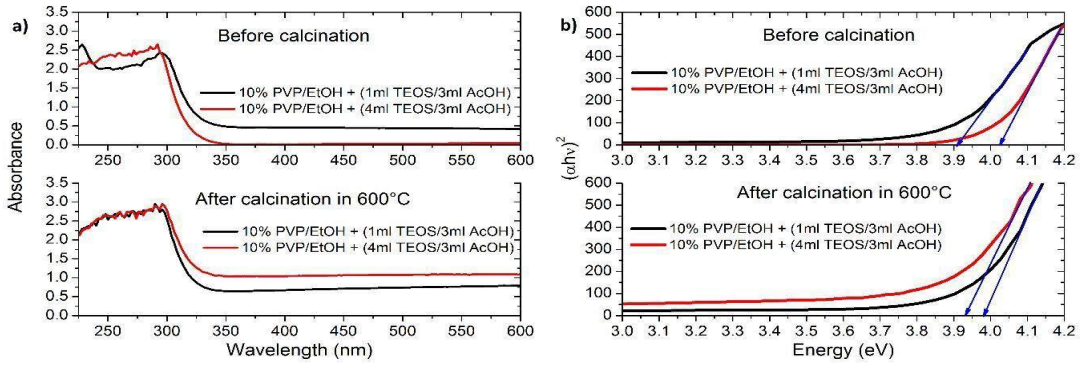

Figure 4 UV-Vis spectrum (a) and dependencies $(\alpha h\nu)^2$ as a function of energy quanta of radiation, along with matching straights, crossing of which with energy axis corresponds to breaks values (b) obtained for the composite nanofibers PVP/SiO2 (before calcination) and nanowires SiO2 (after calcination).

The analysis of energy breaks of the manufactured materials was carried out based on the methodology specified in the works [21, 22]. The assumed value is equal to ½ corresponding to materials with a straight energy break with allowed passages. In the case of composite nanofibers PVP/SiO_2, energy break values were successively 3.91 eV for the fibres obtained from the spinning solution with 1 ml precursor SiO_2, and 4.03 eV for fibres of times greater participation of a precursor (Figure. 4b – before calcination). The carried-out calcination process for the manufactured fibrous composite mats caused the formation of nanowires SiO_2 with energy breaks equal to 3.93 eV and 3.97 eV (Figure. 4b – after calcination in 600°C). The experimental values of energy breaks of the manufactured nanowires of silicon dioxide clearly indicate a broad spectrum of future applications inter alia in electronic industries, substrates of computer chips and solar cells [24].

Exp. Theo. NANOTECHNOLOGY 3 (2019) 269-280

4. CONCLUSIONS

Using the electrospinning method with a solution and sol-gel, nanofibrous composite mats PVP/SiO_2 were obtained, from which nanowires SiO_2 were obtained as a result of calcination at a temperature of 600°C. The analysis of the structure, morphology and chemical composition showed that the final products were clean, amorphous nanowires of silicon dioxide with medium values of diameters at 193 and 155 nm, respectively. The carried out analysis of the optical properties of thin layers of the manufactured nanowires showed a high degree of absorption of electromagnetic radiation of the UV range. In addition, designated energy break values of the tested nanostructures SiO_2, in the order of 3.93 eV and 3.97 eV, suggested that such materials can find a wide range of applications, with particular emphasis put on electronic industries, substrates of computer chips and solar cells.

References

[1] Zhang, H., Liang, C., Liu, J., Tian, Z., Wang, G., & Cai, W. Langmuir 28 (2012) 3938
[2] Faisal, M., Khan, S. B., Rahman, M. M., Jamal, A., & Abdullah, M. M. Applied surface science 258 (2012) 7515
[3] Olson, D. C., Piris, J., Collins, R. T., Shaheen, S. E., & Ginley, D. S. Thin solid films 496 (2006) 26
[4] Ahmed M. A. Hassan, Moustafa Ahmed, M. Nakahama, Fumio Koyama, Exp. Theo. NANOTECHNOLOGY 2 (2018) 91
[5] Huang, M. H., Wu, Y., Feick, H., Tran, N., Weber, E., & Yang, P. Advanced Materials 13 (2001) 113
[6] Lin, Y., Xie, T., Cheng, B., Geng, B., & Zhang, L. Chemical Physics Letters 380 (2003) 521
[7] Liu, Z., Bando, Y., & Tang, C. Chemical physics letters 372 (2003) 179
[8] Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T., & Niihara, K. Langmuir 14 (2003) 3160
[9] Yada, M., Mihara, M., Mouri, S., Kuroki, M., & Kijima, T. Advanced Materials 14 (2002) 309
[10] Bachmann, J., Jing, J., Knez, M., Barth, S., Shen, H., Mathur, S. Journal of the American Chemical Society 129 (2007) 9554
[11] Xu, J., Gao, L., Cao, J., Wang, W., & Chen, Z. Electrochimica Acta 56 (2010) 732
[12] Nishikawa, H., Shiroyama, T., Nakamura, R., Ohki, Y., Nagasawa, K., & Hama, Y. Physical Review B 45(1992) 586

[13] Lin, J., Huang, Y., Zhang, J., Gao, J., Ding, X., Huang, Z., ... & Chen, D. Chemistry of materials 19 (2007) 258
[14] Yu, D. P., Hang, Q. L., Ding, Y., Zhang, H. Z., Bai, Z. G., Wang, J. Applied Physics Letters 73 (1998) 3076
[15] Zong, X., Cai, Y., Sun, G., Zhao, Y., Huang, F., Song, L., ... & Wei, Q. Solar Energy Materials and Solar Cells 132 (2005) 183
[16] Wang, X., Xi, M., Wang, X., Fong, H., & Zhu, Z. Electrochimica Acta 190 (2016) 811
[17] Batool, S. S., Imran, Z., Hassan, S., Rasool, K., Ahmad, M., & Rafiq, M. A. (2016). Enhanced adsorptive removal of toxic dyes using SiO 2 nanofibers. Solid State Sciences, 55 (2005) 13
[18] Lee, E. K., Choi, B. L., Park, Y. D., Kuk, Y., Kwon, S. Y., & Kim, H. Nanotechnology 19 (2008) 185701
[19] Yan, H. F., Xing, Y. J., Hang, Q. L., Yu, D. P., Wang, Y. P., Xu, J. Chemical Physics Letters 323 (2008) 224
[20] An, G. H., Jeong, S. Y., Seong, T. Y., & Ahn, H. J. Materials Letters 65 (2011) 2377
[21] Tański, T., Matysiak, W., Markovičová, L., Florek-Szotowicz, N., Snopiński, P., Krzemiński, Ł., Wiśniowski, M. Journal of Achievements in Materials and Manufacturing Engineering 73 (2015) 165
[22] Tański, T., Matysiak, W. Hajduk, B. Beilstein Journal of Nanotechnology 7 (2015) 1141
[23] Wen, S., Liu, L., Zhang, L., Chen, Q., Zhang, L., & Fong, H. Materials Letters 64 (2015) 1517
[24] Nandanwar, R., Singh, P., & Haque, F. Z American Chemical Science Journal 5 (2015)