The effect of various electrospinning parameter and sol-gel concentration on morphology of silica and titania nanofibers

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Abstract. Nano scale fibers of SiO₂ and TiO₂ with various compositions of viscosity and parameter have been prepared by electrospinning the precursor of tetraethyl orthosilicate (TEOS) and titanium (IV) isopropoxide (TiP). Different concentrations of polymer precursor polyvinylpyrrolidone (PVP) and applied voltages were studied. Distance tip to collector of 15 cm and flow rate of 0.003 mL/h were fixed for entire electrospinning process. The morphology of nanofibers was evaluated versus different solution concentrations as well as different applied voltages. Concentration focused in this study included 5 %wt, 10%wt and 15 %wt of PVP along with 15 kV – 17.5 kV of voltages applied. The as-spun nanofibers were characterized by SEM. Results showed that the average fiber diameter decreases with decreasing of polyvinylpyrrolidone (PVP) solution concentration.

1. Introduction
Titanium dioxide or titania which an inorganic compound with a chemical formula of TiO₂ was laboratory created in late 1800s. This semi-metallic material is produced from ilmenite, rutile, and anatase. It is naturally occurring oxide of titanium which odourless, insoluble and absorbent. Titania is widely used material both as a binder to the fabrication of other products and as a material on its own. With excellent properties, titania is used widely in various applications related to environmental cleaning and protection such as in building painting [1]. Blending titania and paint together may lead to cost reduction of building operation due to its ability to reflect sun light (heat) [2]. Moreover, due to highly oxidizing, cheap and chemically stable, titania is a suited material to be use as photocatalyst to deteriorate air pollutants. In addition, titania nanomaterial is used widely in photovoltaic applications; nanocrystalline TiO₂ film is a core element in dye-sensitized solar cell (DSSC) [3]. Furthermore, titania nanotube has been reported being use as hydrogen sensor on account of its high sensitivity [4].

Silicon dioxide which also called as silica is the most significant material of earth lithosphere with chemical formula of SiO₂. This inorganic compound was first documented as “TiO₂” by Swedish chemist in late 1824. This metalloid compound is colourless/white crystalline and can be found in many
crystalline forms includes α-, β-quartz, α-, β-cristobalite and α-, β-tridymite [5]. Variety applications of silica nanomaterial have been reported nowadays due to it interesting properties. Owing to high melting point, silica (sand) is widely used as core ingredient in manufacturing many engineering related equipment as well as sand casting [6]. Moreover, the correct amount of silica sand improved the strength of cement mixture which make silica as a useful binding component in concrete production [7]. In addition, some publication in nanomedicine describes the use of silica nanomaterial in emerging therapy where silica nanospheres reported being used as Magnetic Resonance Imaging (MRI) contrast agent [8, 9].

Electrospinning represents a simple process of producing nanofibers. It is a unique method to produces ultrafine fibers with a simple setup [10]. The basic apparatus of electrospinning includes a high voltage power supply, pump, syringe, and grounded collector. At the beginning of the electrospinning process, high voltage power is connected to the syringe before the sol-gel is injected. Due to the voltage applied, an electrical field is generated from syringe tip to the grounded collector. As the sol-gel is injected, an electrical repulsive force directs the fiber in form of jet onto the collector [11]. The fibers then calcined at high temperatures to remove the polymer precursor and the desired ceramic phase is obtained. Novel metal oxide (titania) and metalloid (silica) nanofibers have been successfully prepared by electrospinning process [12, 13]. Based on reported studies by Mehran et al. (2018) [14] and Amarei et al. (2017) [15], it is clear that characteristics such as fiber diameter and fiber morphology are strongly depending on the solution concentration.

In the present work, formation of titanium dioxide nanofibers and silicon dioxide nanofibers using the electrospinning technique as well as the effect of solution concentration and apply voltages on nanofiber morphology is investigated.

2. Methods and materials

2.1. Materials
Titanium isopropoxide (TiP) and tetraethyl orthosilicate (TEOS) from Sigma Aldrich was used as the source of titania and silica precursor. For polymer precursor, high molecular weight polyvinylpyrrolidone (PVP) (Mw 1,300,000) was purchased from Sigma Aldrich alongside acetic acid, HCL and ethanol.

2.2. Preparation of Sol-gel
To simplify the condition for analysis, a typical procedure was selected based on previous study. Both silica and titania polymer precursor were prepared by the same procedure. Initially, three different polymer precursor concentrations (5%, 10% and 15%) for both silica and titania were prepared by adding 5 g, 10 g, and 15 g of polyvinylpyrrolidone (PVP) into 10 ml ethanol followed by magnetic stirring for 2 hours at 50 °C with every solution held in a closed beaker. Silica precursor was prepared by mixing TEOS with 3 mL ethanol in a glass beaker followed by adding HCl/water solution to the TEOS/ethanol solution under stirring process. The solution was heated at 80 °C for 30 min and then cooled down to room temperature. Prior to electrospinning, solution was mixed with prepared polymer precursor and undergoes 1 hour stirring process. Titania precursor was prepared by mixing titanium isopropoxide (TiP), 3 mL of acetic acid and 3 mL of ethanol. After a few minutes, the solution then was mixed with prepared polymer precursor and undergoes 1 hour stirring process prior to electrospinning.

2.3. Electrospinning process
Prior to electrospinning process, each solution was loaded into a plastic syringe equipped with a 23-gauge needle. The needle was connected to a voltage supply which is capable of generating DC voltage as high as 25 kV. When concentration was varied, all other parameters were maintained as the following: feeding rate (0.03 mL/min) and electric field strength (17.3 kV). When applied voltage was varied, the polymer concentration was kept at 10%. The distance between the injection orifice and the collector
was kept at 15 cm for all experiments. The relative humidity was controlled between 50 % and 60 % at room temperature throughout the entire electrospinning.

**Table 1. Parameters of electrospinning process.** When solution concentration and applied voltages were varied, all other parameters were maintained.

| Parameter         | Fix                  | Vary             |
|-------------------|----------------------|------------------|
| Syringe           | 23-gauge needle       | -                |
| Feeding rate      | 0.03 mL/min          | -                |
| Distance tip-collector | 15 cm       | -                |
| Concentration     | 10 %                 | 5 %, 10 %, and 15 % |
| Voltage           | 15 kV                | 10 kV, 15 kV, and 17.5 kV |

2.4. **Characterization**
Nanofibers were obtained using scanning electron microscopy (SEM) and Field Emission Scanning Electron Microscope (FESEM) and later morphological studies of fibres before thermal treatment were done employing these images.

3. **Results and discussion**
From the SEM micrographs as shown in Figure 1, it can be observed that beaded fibers formed at low concentration sol-gel of 5 % for both silica (a) and titania (b) electrospun mats. This phenomenon commonly reported when the concentration of the solution used is too low. This is due to the insufficient amount of sol-gel viscoelastic force to overcome the repulsive forces of charge thus resulted on polymer drops on the fibers. The identical phenomenon also reported by Suresh et al. (2005) [16], which they concluded that while polymer tend to have low resistance at low viscosity, surface tension will take place as a major influence on final morphology which may resulted on polymer drops instead of fibers due to high surface tension thus introduced bead formation on the produced fibers. The formation of bead on fiber would significantly reduce surface area hence affect the nanomaterial performance [17]. Beaded fibers were considered as ‘poor’ quality fibers and the electrospinning parameters are often optimized to eliminate beads on fiber.

![Figure 1](image-url)

**Figure 1.** Effect of polymer precursor (polyvinylpyrrolidone) concentration on fiber morphology of silica and titania before calcine at 20 µm (silica) and 5 µm (titania). Silica 5 % (a) and titania 5% (b).

However, beaded fibers are less likely to formed for more viscous solutions. Increase solution concentration will enhance viscoelastic performances of the polymer sol hence able to match the
electrostatic force of electrospinning leading to formation of smooth fibers. When viscosity increased, concentration of polymer solution increased as well due to chain entanglements [18]. Beaded free fiber were obtained for both silica as shown in Figure 2 and titania in Figure 3 at 10 % and 15 % of polymer concentration. Concentrations of 10 % and 15 % polyvinylpyrrolidone of polymer precursor solutions over solvent proved to be the optimum range in order to produce bead-free fibers for both silica and titania nanofibrous mats.

Figure 2. Effect of polymer precursor (polyvinylpyrrolidone) concentration on fiber morphology of silica and titania before calcine at 20 µm (silica) and 5 µm (titania). Silica fibers at 10 % (a) and 15 % (b) PVP concentration. Titania fibers at 10 % (c) and 15 % (d) PVP concentration.

The data in Figure 3 show trends for nanofibers diameter when PVP concentration become higher for both silica (a) as well as titania (b). 5 % polymer concentration of silica nanofiber (a) have an average fibers diameter of 110 nm. These diameter value then increased to 174 nm at 10 % polymer concentration and 210 nm at 15 % concentration. Titania (b) electrospun nanofiber also have identical phenomenon, where it can be observed that average fibers diameter of 5 % polymer concentration (125 nm) increased to an average of 166 nm (10 %) and 253 nm (15 %). The increments of polymer concentration would lead to several affect includes increases of polymer chain entanglements [16]. This phenomenon leading to thicker injected polymer from syringe thus increase the collected fiber diameter on grounded collector surface. Based on the literatures, removal of polyvinyl alcohol by calcination process of 500 °C will reduce the fiber diameter by an average of 80 nm [13, 19]. From this statement, an assumption was made and represented by the solid line (below) in Figure 3 for both silica (a) and titania (b). It can be observed that polymer concentration have significant effect on pure silica and titania
fiber diameter after calcination process. Increased in polymer concentration not only will increased fiber diameter before calcination but as well as pure fibers after removal of polymer precursor. When concentration is varied with fixed parameters in electrospinning, the volume of entrapped fiber precursor depends on volume of injected polymer, signifying that as the polymer become more concentrated it will resulted on the bigger fiber diameters [20].

![Figure 3](image1.png)

**Figure 3.** Effect of PVP solution concentration for silica (a) and titania (b) on fiber diameter before calcine. Solid line (below) represents an assumption of calcined fiber diameter.

Adjusting the voltage applied have numbers of impacts on the electrospinning process. Increasing voltage will accelerate the electrospinning jet and this may result in larger volume of solution drawn from the tip of the needle. One of the impacts found resulted on increasing the applied voltage is reduction of fibers diameters. In this study, increasing the apply voltage resulted on the non-uniform fiber diameter distribution between 120-160 nm. These non-uniform fiber distribution was reported as the result of branching jet [21]. Accordingly, the distribution of non-uniform diameter of fibers in this study may resulted from branching jet during electrospinning process. However, fiber breakage is the most significant impact resulted from varying the applied voltage. As shown in Figure 4, fibers obtained at 10 kV appear broken whereas the fibers obtained at 15 kV and 17.5 kV are continuous. It can be concluded that applied voltage of 10 kV was not enough to produce continuous nanofibers from the solution at the given concentration.

![Figure 4](image2.png)

**Figure 4.** Effect of voltage applied on fibers morphology with polymer concentration at 10 % and fixed other electrospinning parameters. (a) 10 kV, (b) 15 kV, (c) 17.5 kV.
4. Conclusion
In this work, the effect of PVP solution concentration on electrospun silica and titania fibers in terms of the morphologies has been explored. It was found that the properties of electrospun silica and titania fibers fabricated is critically depending on the electrospinning parameters such as PVP solution concentration. With decreasing the PVP solution concentration, the fiber diameter decreases. Beaded fiber structure was obtained at lower polymer concentration 5% but an increase in the polymer concentration to 10% and 15% yielded bead free fibers, which indicates that a high viscosity is required to obtain uniform Silica and Titania nanofibrous mats. In addition, voltages apply at the given concentration.

5. References
[1] Xiaobo Chen and Samuel S. Mao 2007 Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications Chem. Rev. 107(7) 2891–2959.
[2] Shuang Shi, Dongya Shen, Tao Xu and Yuqing Zhang 2018 Thermal, optical, interfacial and mechanical properties of titanium dioxide/shape memory polyurethane nanocomposites Composites Sci. and Technol. 164 17-23.
[3] Boschloo Gerrit 2019 Improving the performance of dye-sensitized solar cells Front. Chem 7 77.
[4] Bertuna A, Comini E, Poli N, Zappa D and Sberveglieri G 2016 Titanium dioxide nanostructures chemical sensor Procedia Engineering 168 313-16.
[5] Huahai Mao, Sundman B, Zhongwu Wang and Saxena S K 2001 Volumetric properties and phase relations of silica - thermodynamic assessment J. of Alloys and Compounds 327(1-2) 253-62.
[6] Potapov V, Serdan A, Gorev D, Zubaha S and Shunina E 2019 Colloid silica in hydrothermal heat carrier: characteristics, technology of extraction, industrial applications IOP Conf. Ser.: Earth Environ. Sci. 249 012043.
[7] Esfandiar J and Loghmani P 2019 Effect of perlite powder and silica fume on the compressive strength and microstructural characterization of self-compacting concrete with lime-cement binder Measurement 147 106846.
[8] Kathryn M. L. Taylor, Jason S. Kim, William J. Rieter, Hongyu An, Weili Lin and Wenbin Lin 2008 Mesoporous silica nanospheres as highly efficient MRI contrast agents J. Am. Chem. Soc. 130(7) 2154–55.
[9] Yan Chen, Kelong Ai, Jianhua Liu, Guoying Sun, Qi Yin and Lehui Lu 2015 Multifunctional envelope-type mesoporous silica nanoparticles for pH-responsive drug delivery and magnetic resonance imaging Biomaterials 60 111-120.
[10] Nandana Bhardwaj and Subhas C. Kundu 2010 Electrospinning: A fascinating fiber fabrication technique Biotecnol. Adv. 28(3) 325-47.
[11] Gregory C. Rutledge and Sergey V. Fridrikh 2007 Formation of fibers by electrospinning Adv. Drug. Deliv. Rev. 59(14) 1384-91.
[12] Alves A K, Berutti F A, Clemens F J, Graule T and Bergmann C P 2009 Photocatalytic activity of titania fibers obtained by electrospinning Mater. Res. Bulletin 44(2) 312-17.
[13] Li Zhang, Qinghong Zhang, Hongyong Xie, Jiang Guo, Hailong Lyu, Yaogang Li, Zhiguo Sun, Hongzhi Wang and Zhanhu Guo 2017 Electrospun titania nanofibers segregated by graphene oxide for improved visible light photocatalysis Appl. Catal. B: Environ. 201 470-8.
[14] Mehran Shahhosseininia, Saeed Bazgir and Morteza Daliri Joupari 2018 Fabrication and investigation of silica nanofibers via electrospinning Mater. Sci. and Eng. C 91 502-11.
[15] Amariei N, Manea L R, Bertea A P, Bertea A and Popa A 2017 The influence of polymer solution on the properties of electrospun 3D nanostructures IOP Conf. Ser.: Mat. Sci. and Eng. 209 012092.
[16] Suresh L. Shenoya, Wm Douglas Batesa, Harry L. Frischb and Gary E. Wneka 2005 Role of chain entanglements on fiber formation during electrospinning of polymer solutions: Good solvent, non-specific polymer-polymer interaction limit Polymer 46(10) 3372-84

[17] Adnan Haider, Sajjad Haider and Inn-Kyu Kang 2018 A comprehensive review summarizing the effect of electrospinning parameters and potential applications of nanofibers in biomedical and biotechnology Arabian J. of Chem. 11(8) 1165-88.

[18] Jason Swei and Jan B Talbot 2003 Viscosity correlation for aqueous polyvinylpyrrolidone (PVP) solutions J. of Appl. Polymer Sci. 90(4) 1153-55.

[19] Susan V Olesik and Toni E. Newsome 2014 Electrospinning silica/polyvinylpyrrolidone composite nanofibers J. of Appl. Polymer Sci. 131(21) 40966.

[20] Hamid Esfahani, Rajan Jose and Seeram Ramakrishna 2017 Electrospun ceramic nanofiber mats today: Synthesis, properties, and applications Materials 10(11) 1238.

[21] Yarin A L Kataphinan W and Reneker D H 2005 Branching in electrospinning of nanofibers J. of Appl. Phys. 98 064501.

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