# ELECTROSPINNING OF SILICA NANOFIBERS: CHARACTERIZATION AND APPLICATION TO BIOSENSING

A Thesis

by

PEI-HSIANG TSOU

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2006

Major Subject: Electrical Engineering

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Approved by:

| | |
|---|---|
| Chair of Committee, | Jun Kameoka |
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# ABSTRACT

Electrospinning of Silica Nanofibers: Characterization and

Application to Biosensing. (August 2006)

Pei-Hsiang Tsou, B.S., National Chiao Tung University, Taiwan

Chair of Advisory Committee: Dr. Jun Kameoka

Electrospinning is a technique to achieve nanometer scale fibers. Similar to the conventional spin methods of making fabric, the viscous polymer solution is ejected from a spinneret; stretched and solidified in the air, the solution forms the fibers. The different part of electrospinning among others is that the fibers are driven by the electrostatic force, which induces the repulsion inside the liquid and further reduces the diameter. The resultant product is a non-woven membrane, which is porous; and the pore size is around several nanometers to a micrometer wide.

In this work, the relationship between the diameter of electrospun silica fibers, experimental parameters such as concentration and voltage, and between pore size of the fiber membrane and experimental time were studied. Materials used in the process are Polyvinylpyrrolidone (PVP), butanol and spin-on-glass coating solution, which act as polymer carrier, solvent, and silica-precursor, respectively. Polymer/silica precursor composite fibers were ejected from the needle of a plastic syringe when an electrical field, as high as several kV/cm, was applied. Then silica fibers were achieved by baking the composite ones at 773 $^{o}$K for 12 h. Electrospun silica nanofibers were characterized

as a function of polymer solution parameters. The calcined fibers were examined by using a field emission scanning electron microscope. The results showed that the fiber diameters decrease with decreasing proportion of polymer and silica precursor, and increase with a higher electric field. Pore sizes, defined as the grid areas enclosed by fibers on nearby layers, were also examined and showed no time-dependent tendency when the electrospin time was between 1-5 min. Fiber membranes were then used as the platform for protein detection. The results were compared with the control, which used glass slides as the platform. The results make it possible to make a more sensitive biosensing device.

# ACKNOWLEDGMENTS

I would like to thank my committee chair, Dr. Jun Kameoka, for his valuable guidance and constant encouragement through the course of this research. I would like to thank my committee members, Dr. Chanan Singh, Dr. Christi K. Madsen, and Dr. Kenith Meissner, for reviewing my thesis and giving me useful comments.

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Finally, I would like to express my gratitude and share my happiness with my parents, whose support and encouragement made the research enjoyable.

# NOMENCLATURE

| | |
|---|---|
| ELISA | Enzyme-Linked Immunosorbant Assay |
| PVP | Poly(vinyl pyrrolidone) |
| SEM | Scanning Electron Microscope |
| SOG | Spin-On-Glass Coating Solution |

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# 1. INTRODUCTION

One-dimensional nano-materials have attracted people's attention for their various application possibilities: composites, protective clothing, catalysis, electronics, biomedicine, filtration, agriculture, etc.[1, 2-5] In order to accommodate different purposes, many fabrication methods have been invented, such as vapor-liquid-solid growth and solution-liquid-solid growth (for Si, InP, InAs, GaN, etc), template based synthesis (for Sn, Bi, etc), chemical vapor deposition (for carbon nanotubes), and electrospinning (for polymers).[6-9] Compared to all other methods, electrospinning is a more effective way to fabricate relative long and continuous polymer-based fibers.

The way to produce electrospun fibers is very similar to traditional fiber spinning methods. For example, in dry spinning and melt spinning, the polymer solution or polymer melt is forced to pass through a spinneret and form multi-liquid threads. The threads are then exposed to hot air to get rid of solvent, or a cooler environment, to solidify. (Figure 1) In electrospinning, fibers are drawn by electrostatic forces and are produced through a capillary.

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This thesis follows the style of *Nano Letters.*

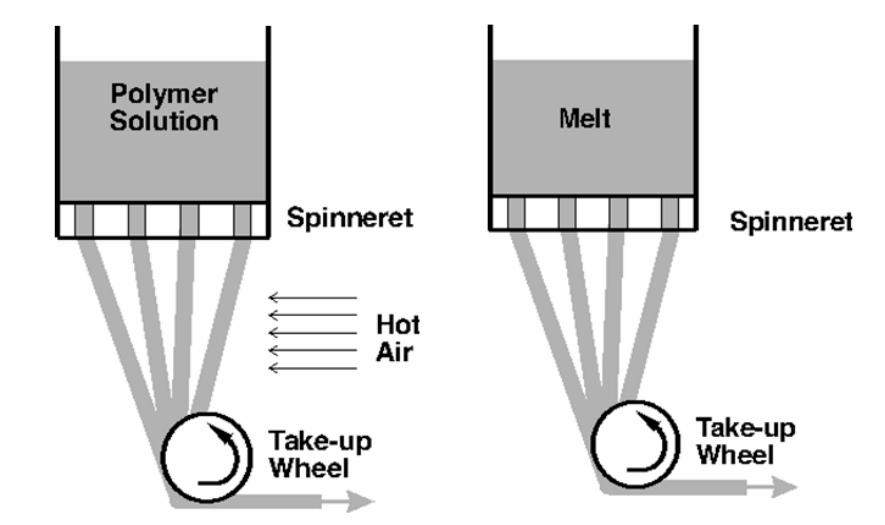


Figure 1. Concepts of dry spinning and melt spinning methods.[10]

Two common electrospinning setups are shown in Figure 2. The process includes loading the polymer solution into a syringe fixed on a syringe pump, attaching the positive electrode to the needle, adjusting the distance between the needle tip and a grounded collector, pumping, and increasing the voltage until the polymer jets appear.[9] Though detail mechanisms are still investigated by researchers, the principle of the phenomena is using strong electrical field to overwhelm the surface tension of the polymer solution at the needle tip. While the polymer is ejected, the fast evaporation of the solvent solidifies the liquid jets and forms an extremely thin fiber. The diameters of the electrospun fiber vary from micrometers to nanometers, depending on the selection of polymers, electrical fields, pumping rates, and other environmental factors.[11] In addition to electrospun pure polymer fibers, metal oxides fibers can also be produced by

adding metal oxide precursors into the polymer solutions, electrospinning, and removing the polymer parts by baking at high temperature. The polymers in the above methods play as the fiber templates, so the resultant metal oxide fiber diameters can be further reduced.[12-14]

In this study, the silica fiber membranes were electrospun by using the above methods. Physical features were studied, which included the relationship between (1) fiber diameter and polymer concentration; (2) fiber diameter and applied voltages; (3) fiber diameter and the concentration of the silica precursor; (4) pore sizes and experimental time. Fiber membranes were then used as the platform for molecular detection. The results were compared with which performed on glass slides. From the results, it is possible to make a more sensitive molecular-detection device, which can improve the well-known Enzyme-Linked Immunosorbant Assay (ELISA).

(A) (B)

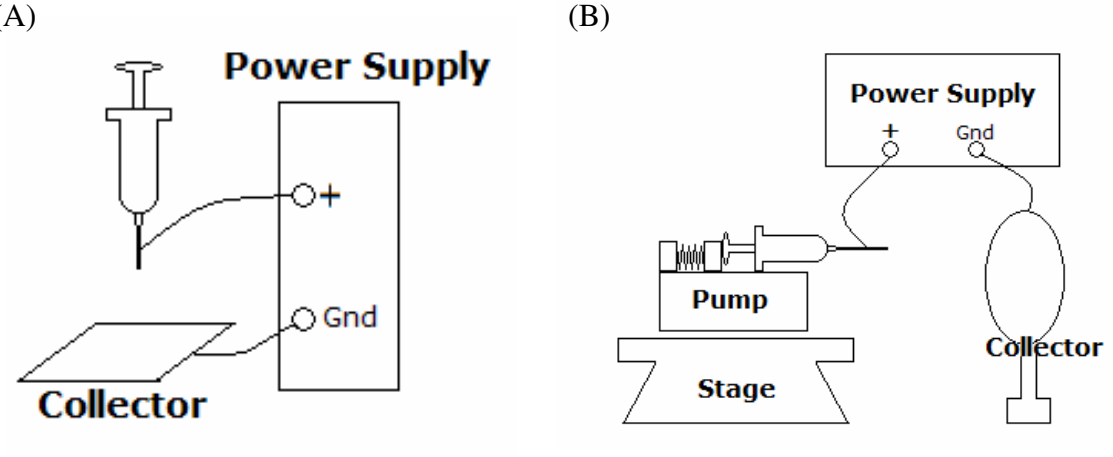


Figure 2. Two typical experimental setups of electrospinning. (A) Vertical setup; (B) horizontal set up.

# 2. BACKGROUND

## 2.1 Electrospinning

The history of electrospinning can date back to 1934, when Anton Formhals patented a device to collect the electric field-induced polymer threads.[15] In his design shown in Figure 3, solution mixed with cellulose acetate, alcohol, acetone, and softening agent was brought by a serrated wheel, and spun on a charged rotating metal ring. The spun threads were even washed, dried and stretched. However, it still cannot rival other more efficient spinning methods and the mass production requirement at the same time. Not many people noticed the technique in the following decades. It is not until 1990's, when Dr. Reneker and some contemporary researchers investigated the process and its potential in nanotechnology, that electrospinning began to attract people's attention and be studied.[16] Several kinds of materials have been tried, including synthesis fibers such as polyethylene oxide (PEO), nylon, polyvinyl alcohol (PVA), polyurethane (PU), liquid crystal like polyphenylene, polyaniline, and natural material such as silk from silkworms or spiders, DNA, etc.[9]

The specialties of electrospinning include its possibilities of producing long and continuous nanometer-scale fibers, extremely large surface-to-volume ratio of the electrospun nonwoven, and the molecular-level alignment. The large surface area is especially favorable for many applications such as biomedical scaffolds, catalysts, or sensors.[16]

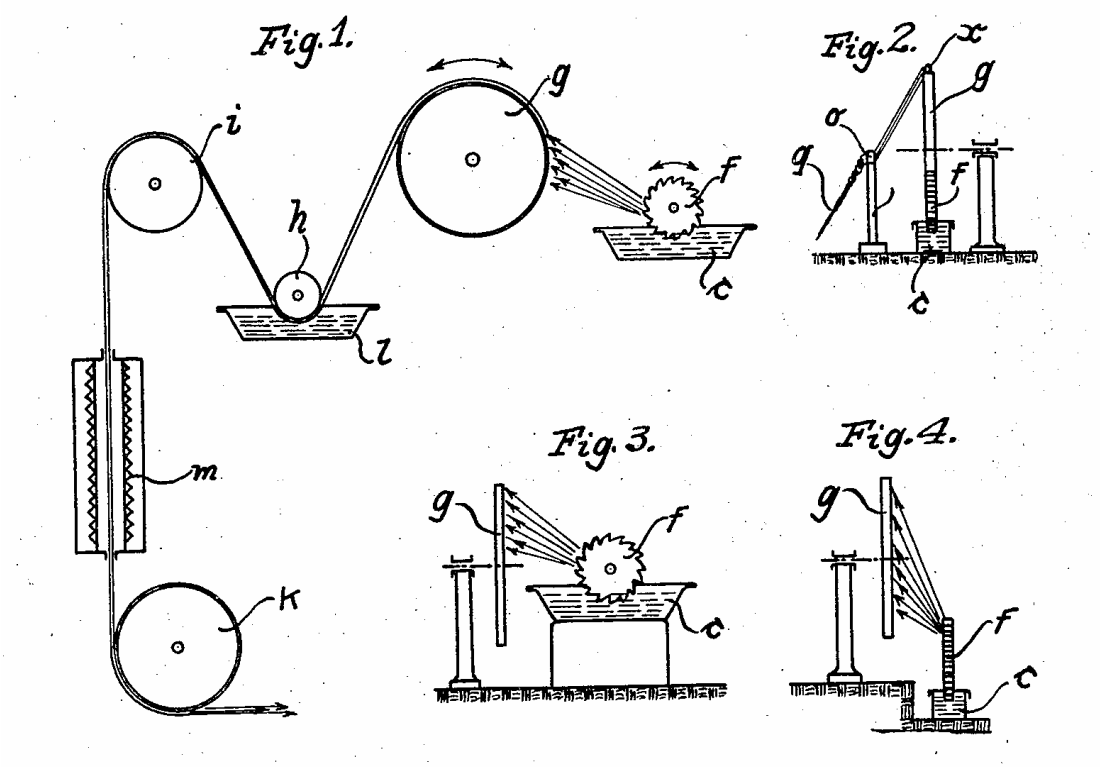


Figure 3. Anton Formhals' design for collecting the electrospun threads patterned in 1934. The solution *i* was provided by rotating serrated wheel *f* and spun to wheel *g*, then transferred to washing device *h*, drying device *m*, and stretching device *k*.[15]

The setup of electrospinning has been introduced in the previous section. It can be performed in any direction, since the solution is mainly attracted by the electrostatic force. Once the solution emerges from the tip, the curvature of the droplet changes. The hemispherical droplet elongates and forms a conical shape, known as the Taylor cone, and then ejects out of the needle.[17] Depending on the setup parameters, what deposits on the collector can be fibers, beads, or mixtures of them. (Figure 4) The fibers take shape

when the solvent evaporates before landing on the collector. Instead of direct aggregating on a spot, liquid jet is stretching and whipping, which are the features that make fibers extremely thin.[11]

For years, people have tried to fabricate thinner fibers through electrospinning. Controllable parameters for same materials involve (1) electric field (kV/cm) between the nozzle and the collector; (2) flow rate (μL/min), the supply rate of the spun solution; (3) deposition distance (cm), the distance between the needle tip and the collector; (4) concentration, such as polymer concentration or concentration of other solutes. Typical relationships between fiber diameter and process parameters can be described as the plots in Figure 5. Deposition distance affects the amount of the solvent evaporated before fibers are collected, which influences the degree of fiber shrinkage. Electric field affects the charge distribution of liquid jets and the electrostatic force pulling the jets. Larger electric field causes stronger repulsive force in the charged liquid jet, forcing them to stretch. Flow rate restricts the volume of liquid emerged at the tip per unit time. When the volume is smaller, more mutual repulsion occurs and fibers are extracted further. Concentration here means polymer concentration, and it decides the degree of polymer chain entanglement. Viscous solution has more entanglement, and then more resistance to counter the stretch. Thin fibers can be achieved by lowering the concentration of polymer. However, a critical value has to be satisfied to prevent the liquid jet broken. If silica precursor is used in electrospinning, concentration of precursor also affects the diameter. It decides how much amount of silica will remain after the baking. The more the precursor, the thicker the fibers.

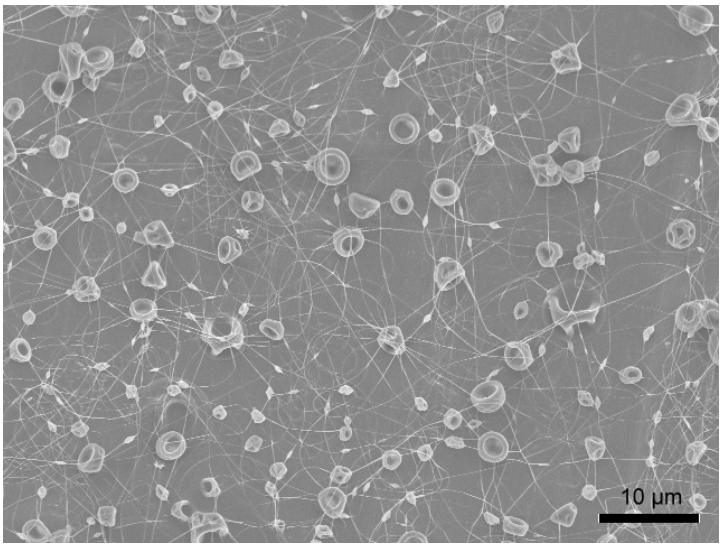


Figure 4. The mixture of beads and fibers. The parameters are: PVP 0.02 g/mL, SOG:butanol=100:0, flow rate 8 µL/min and the spun distance 5 cm.

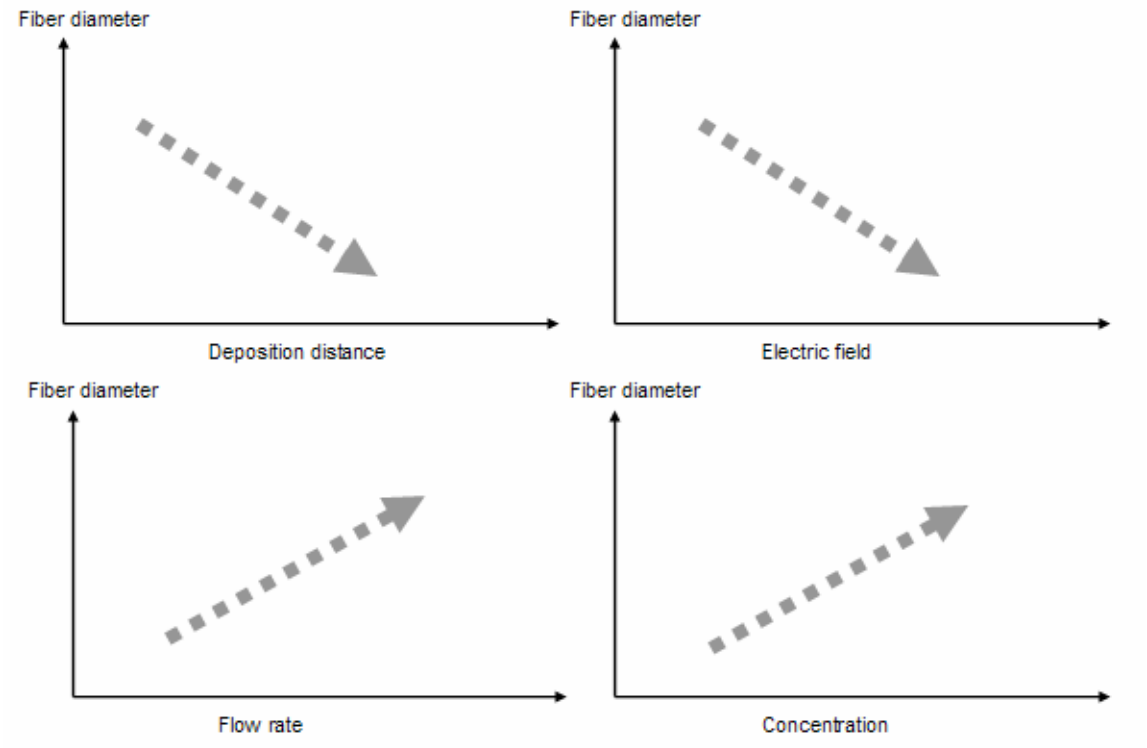


Figure 5. Typical relationships between fiber diameter and main parameters.

The associated applications of electrospun nanofibers are various: nylon fibers can be incorporated into bulk epoxy resin to increase the stiffness and mechanical strength of the material;[19] electrospun membranes have been used to separate aerosol for years; poly(e-caprolactone) (PCL) fiber membranes can play as biomedical scaffolds to improve tissue growth;[16] Poly(vinyl alcohol) fiber membranes can supports enzymes and control the release rate;[17] electrospun polyaniline/PEO fibers less than 100 nm have conductivities which is dependent on the diameters; uniaxially aligned PVP nanofibers can act like light polarizers;[20] heat depolymerizable polycarbonate nanofibers can be used as sacrificial templates to produce nanofluidic channels;[21] electrospun polyaniline/poly-(ethylene oxide) (PANI/PEO) nanowire sensors can detect ammonia gas at very low concentration.[22]

This thesis focused on the application in molecular detection, especially for the detection of protein like antigens and antibodies. The property of large surface area of nanofiber membranes is used to improve the sensibility of a traditional detection method called ELISA, which is introduced in the following section.

## 2.2 Enzyme-Linked Immunosorbant Assay (ELISA)

ELISA is a technique that can detect proteins, and hormones. It bases on the fact that antigens and their corresponding antibodies will form a strong complex when they contact. In human bodies, antibodies are released by B-cells when B-cells detect antigens such as bacteria or virus. Although many kinds of antibodies can be produced, each antibody can only recognize one specific receptor on the surface of antigens. Once

a certain kind of antibodies is binding to the receptors, immune defense is triggered, and T-cells will come to destroy the antigen. Therefore, the presence of antibodies can be an indicator of some known diseases, since the antibodies can appear the characteristics of disease-related antigens. Among all assays of detecting antibodies, ELISA has the advantages of fast and accurate since introduced in 1971.[18, 23-25] ELISAs are performed in 96-well or 384-well polystyrene plate. Steps of ELISA are listed as follows:

(1) Coat antigens (to detect antibodies) or antibodies (to detect antigens) on the inner surface of each well. The antigens or antibodies stick on the surface due to the Van der Waals force. Add blocking agents to block the unoccupied areas of the well to prevent unwanted binding of other molecules.

(2) Add the sample and incubate the mixture for 15 minutes. This makes the antibodies and antigens react completely.

(3) Drain out the solution from each well and wash the well 3 to 6 times by buffer solution to remove excess antibodies or antigens that do not react.

(4) Add secondary antibodies, antibodies linked with detection enzymes HRP, and incubate the mixture for 15 minutes for completely reaction. The secondary antibodies only attach the target antibodies or antigens, and HRP (horseradish peroxidase) is an enzyme that can stimulate the conversion of the colorless substrate into a colored product.

(5) Remove the solution from each well and wash the well 3 to 6 times, same as (3).

(6) Add HRP-substrate. The HRP enzyme attached to the secondary antibody will catalyze the substrates and change the color of HRP-substrate. Researchers can

know the existence of target antibodies or antigens by observing the color.

(7) Wait for 15 minutes and observe the color by using ELISA detector.

Since ELISA can detect both antigens and antibodies, it is called direct ELISA for the assay used in the detection of specific antigens, and called indirect ELISA for which used in the detection of specific antibodies (Figure 6, Figure 7).

The signal strength of ELISA is related to the surface area of each well, since the detection relies on trapping the target protein by the pre-coated antigens or antibodies on the surface. Protein can easily attach to any surface due to the Van der Waals force between the protein and the surface, if they can get enough close to the surface. However, not all target protein, antigens or antibodies, in the solution can participate in the reaction. Some of them are washed away before wandering to the surface of the well. If the concentration is extremely low, the condition worsens since almost no molecule can attach to the surface. One solution to these problems is to pour the solution into a filter-like device made of nanofibers. This kind of device has at least two advantages. First, the nanofibers' large surface area can contain much more "catcher" molecules and provide more exposure area for the sample. Second, the sample is forced to pass the structure, and fewer molecules will escape. The above idea is practiced in the experimental part.

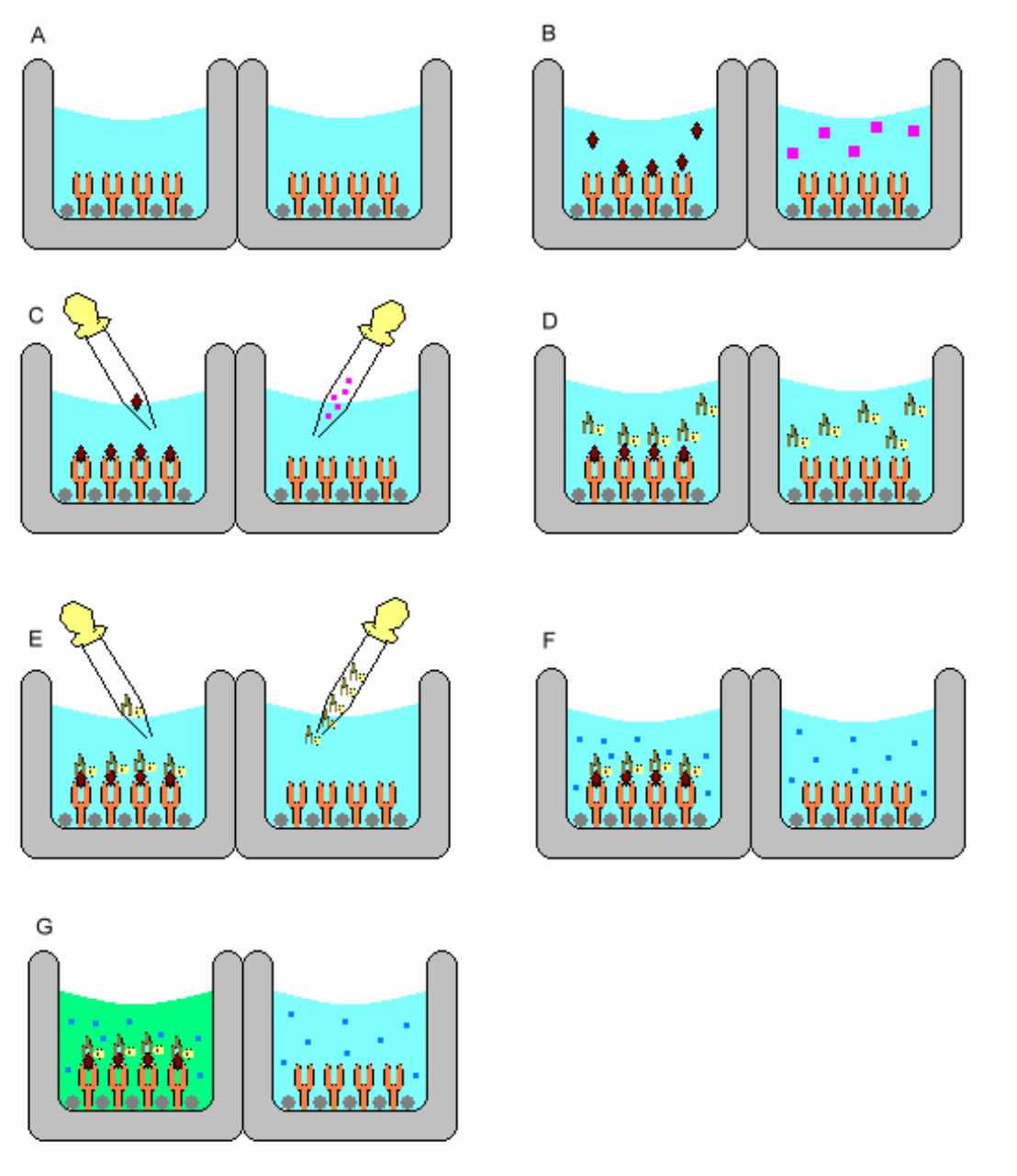


Figure 6. The steps of direct ELISA. (A) antibodies (Y-shape) are coated on the ELISA wells, followed by filling the unoccupied sites with blocking agents (grey circle); (B) antigens join and only complementary ones (black diamonds) will attach to the antibodies; (C) unbound antigens are removed; (D) antibodies with detection enzymes join and bind to the target antigens; (E) unbound antibodies are removed; (F) substrate joins the reaction; (G) solution changes color if having target antigens.

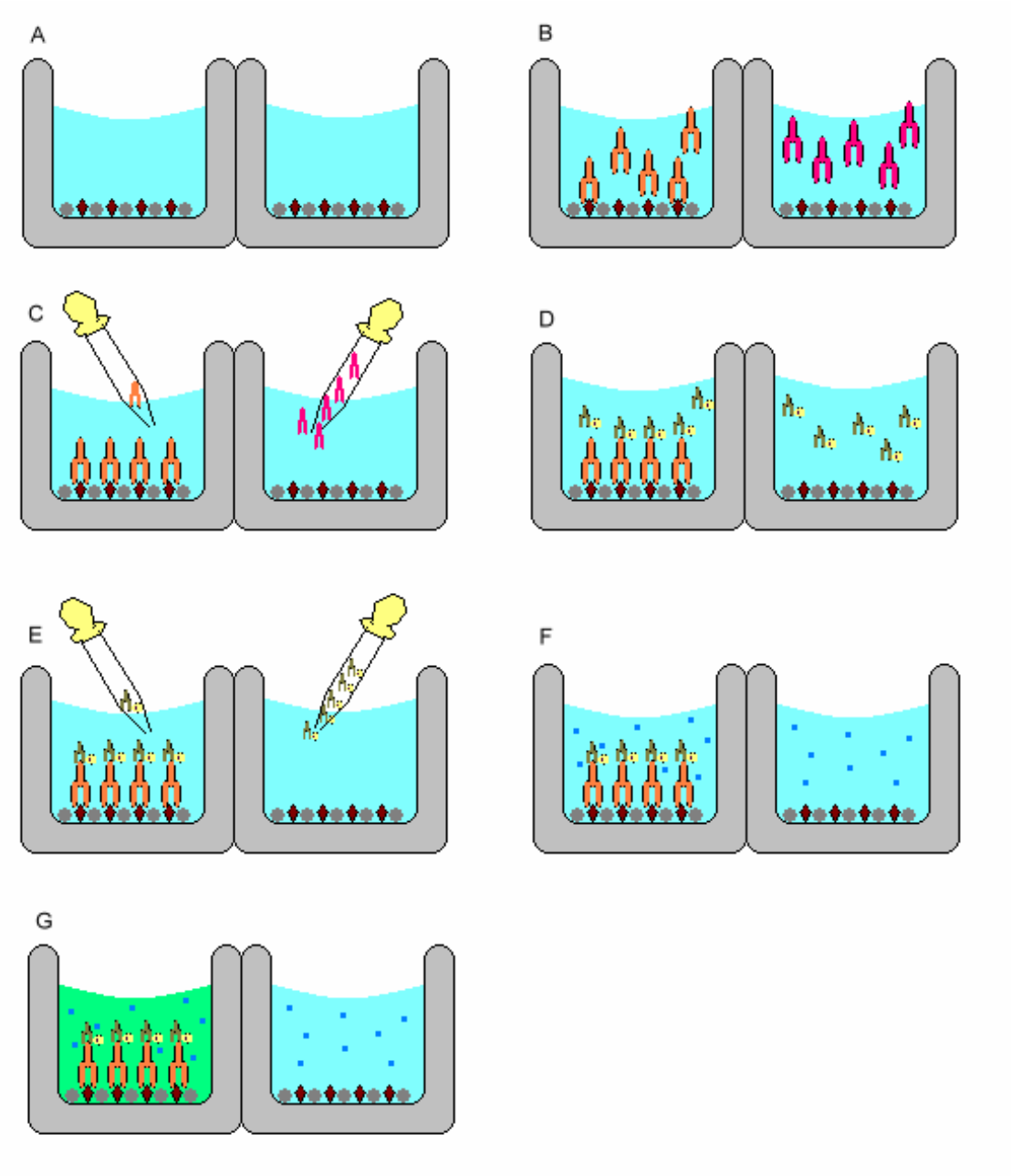


Figure 7. The steps of indirect ELISA. (A) antigens (black diamonds) for target antibodies are coated on the ELISA wells, followed by filling the unoccupied sites with blocking agents (grey circles); (B) antibodies join and only complementary ones (orange Y-shapes) will attach to the antigens; (C) unbound antibodies are removed; (D) antibodies with detection enzymes join and bind to the target antibodies; (E) unbound antibodies are removed; (F) substrate joins the reaction; (G) solution changes color if having target antibodies.

# 3. EXPERIMENTAL

The goals of the experiments are to find (1) how voltage and solute concentration affect the diameter of fibers; (2) how time factor affects the pore size of membranes; (3) the practicability of using the electrospun membrane as a molecular detection device. The first two goals will provide possible references for fabricating small diameter nanofibers and filtration devices; the third goal will help to improve the sensitivity of molecular detection devices. The solution used in the experiments has three ingredients: polymer PVP, silica precursor SOG, and the solvent butanol. Some parameters, such as PVP concentration and electric field, are based on a journal article that studied titania nanofibers.[7]

## 3.1 Material Data

The chemicals and equipments used in the characterization experiment are listed in following table. (Table 1) The mixture of PVP, SOG, and butanol is not toxic but may cause stimulating odors; it is recommended to wear masks and perform the experiments in ventilated environment.

Table 1. Material data of the electrospinning experiments.

| Chemicals/Equipments | Specification |
|---|---|
| Poly(Vinyl Pyrrolidone) (PVP) | MW=1 300 000, Aldrich |
| Spin-on-Glass Coating Solution | IC1-200, Futurrex, Inc. |
| Butanol | Solvent Diluent SD4,Futurrex, Inc. |
| Magnetic Stirrer | |
| High Voltage Power Supply | Series 230, Bertan |
| Syringe Pump | Syringe Pump 11 plus, Harvard Apparatus |
| Furnace | Isotemp Muffle Furnace 550, Fisher Scientific |
| Balance | Scout Pro SP202, Ohaus Corporation |
| Scanning Electron Microscope | Leo 1530VP, Zeiss |
| Collector | Covered by aluminum foil 10 cm in diameter |
| Adjustable Stage | 271/281 Series High Load Lab Jacks, Newport |
| Plastic Syringes | BD 10 mL Syringe |
| Stainless Steel Needles | 24 Gauge |
| Tweezers | |
| Masks | |
| Gloves | |

3.2 Procedures

Preparing proper solutions is a crucial part for each experiment, since the proportion of solute and solvent will affect the formation of spun fibers. Three components are in a solution: solid PVP, liquid SOG, and liquid butanol. The solvent is the total amount of butanol, includes some butanol in liquid SOG.

Some definitions are used in this thesis:

$$\text{PVP concentration (g/mL)} \equiv \frac{\text{Weight of PVP (g)}}{\text{Total volume of SOG and butanol (mL)}}$$

$$\text{SOG volume concentration (\%)} \equiv \frac{\text{Volume of SOG (ml)}}{\text{Total volume of SOG and butanol (ml)}}$$

Electrospun time (sec) ≡ The time duration of applied high voltage during electrospinning

Pore sizes (nm) ≡ The estimated diameter of a virtual particle which can pass the area surrounded by fibers within adjacent layers

3.2.1 Fiber Diameter versus Polymer Concentration and Applied Voltages

(1) The solutions with PVP concentration 0.02 g/mL, 0.03 g/mL, 0.04 g/mL, 0.05 g/mL and 0.06 g/mL were prepared by adding different quantities of solid PVP to SOG solution 4 mL, followed by magnetic stirring for 24 hours.

(2) Electrospinning began under the following parameters mentioned before: pumping rate 8 μL/min and the spun distance 5 cm.

(3) After the liquid flow rate was stable, fiber membranes were collected on pieces of aluminum foil at 3 kV, 4 kV, 5 kV, 6 kV and 7 kV respectively for one minute.

(4) The samples were transferred to the furnace and baked at 773 k for 12 hours.

(5) Samples and their diameters were observed and measured by using the SEM. The steps about using SEM is in section 3.2.5.

(6) Relationship was plotted according to the calculated average and standard deviation.

3.2.2 Fiber Diameter versus Silica Precursor Concentration and Applied Voltages

(1) The solutions with SOG volume concentration 20%, 40%, 60%, and 80% were prepared by adding 0.4 g solid PVP to diluted SOG solution 10 mL, followed by magnetic stirring for 24 hours.

(2) Electrospinning began under the following parameters mentioned before: pumping

rate 8 μL/min and the spun distance 5 cm.

(3) After the liquid flow rate was stable, fiber membranes were collected on pieces of aluminum foil at 3 kV, 4 kV, 5 kV, 6 kV and 7 kV respectively for one minute.

(4) The samples were transferred to the furnace and baked at 773 k for 12 hours.

(5) Samples and their diameters were observed and measured by using the SEM.

(6) Relationship was plotted according to the calculated average and standard deviation.

3.2.3. Pore Size versus Spin Time

(1) The solution having SOG volume concentration 80% and PVP 0.04 g/mL in 3.2.3 was used in this experiment.

(2) Electrospinning began under the following parameters mentioned before: voltage 7 kV, pumping rate 8 μL/min, and the spun distance 5 cm.

(3) After the liquid flow rate was stable, fiber membranes were collected on pieces of aluminum foil for 1 minute, 2 minutes, 3 minutes, 4 minutes, and 5 minutes respectively.

(4) The samples were transferred to the furnace and baked at 773 k for 12 hours.

(5) Samples and their pore sizes were observed and measured by using the SEM.

(6) Relationship was plotted according to the calculated average and standard deviation.

3.2.4 Hybridization Test

The goal of the test is to see if more proteins, such as antigens and antibodies, can attach to the nanofiber membranes than the results using a glass slide. Typically, antigens and

antibodies can attach to any surface due to the Van der Waals force between proteins and the surface. Nanofiber membranes are expected to attract more because of their large surface area. The test steps are listed as follows:

(1) As in Figure 8, two glass slides were prepared. Two silica fiber membranes were attached on one glass slide; nothing was placed on the other glass slide.

(2) 10 μL protein A (BSA, 1 μg/μL) and 10 μL protein B (mouse anti-flag antibody, 1 μg/μL) were coated on fiber membranes and the other glass slide, respectively.

(3) Slides were coated with blocking agents (10% Fetal Bovine Serum) for 30 min in room temperature. The molecules fill the unoccupied areas of the surface.

(4) Slides were washed by buffer solution (PBS, phosphate-buffered saline) for 5 minutes to remove non-binding antibodies.

(5) Protein C (goat anti mouse antibody-HRP, the secondary antibody conjugated with detectable signal and will only bind to protein B) was applied on both slides for 30 min in room temperature.

(6) Slides were washed by buffer solution (PBS, phosphate-buffered saline) for 4 times, 10 minutes per time, in room temperature.

(7) Add HRP-substrate and detect the signals.

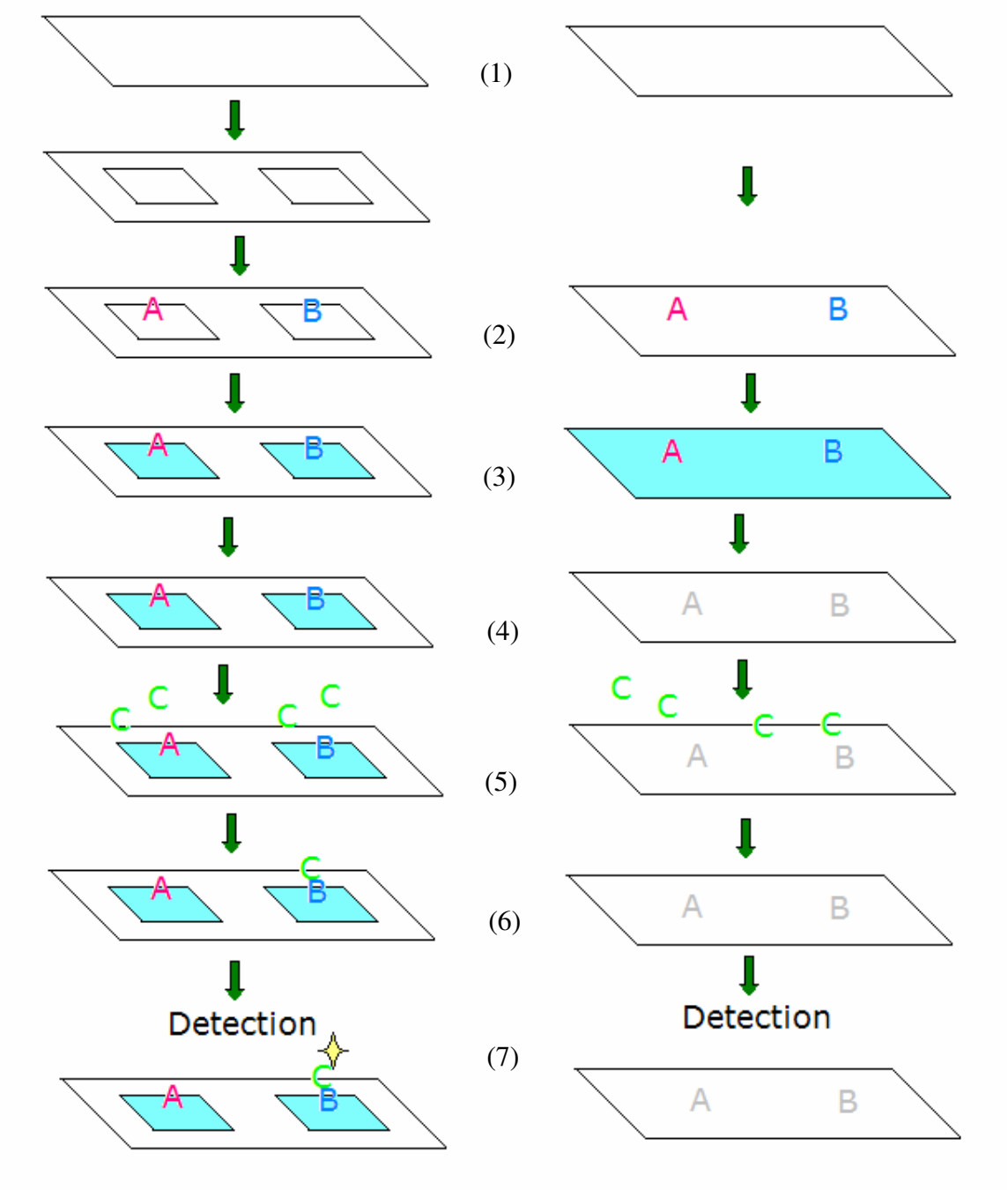


Figure 8. Procedures of hybridization test. The numbers follow the steps described in the statement.

3.2.5 SEM Procedure

(1) Scanning electron microscope, Zeiss 1530 VP FE-SEM, in the Microscopy and Imaging Center (MIC) was used in this thesis. Each sample was attached on a 1-cm-diameter stubs by the carbon tape.

(2) Samples were coated with a platinum layer 3 nm thick before observation.

(3) The chamber of the microscope was vented until the chamber door could be opened.

(4) Samples were placed and fixed by screws. The chamber was vacuumed until the pressure reached to less than $10^{-5}$ torr.

(5) The electron gun was set 5 kV and turned on.

(6) Once the target sample was located, working distance (focal length) was set 3~5 mm.

(7) Associated parameters such as brightness, contrast, magnification, stigmation, and aperture alignment were tuned to best imaging. Images were collected under 5 kX ~ 40 kX magnification, depending on the size of the fibers or pores.

(8) Fiber diameters or pore sizes were measured by using the function embedded in the SEM software. Twenty figures were collected for each sample.

# 4. RESULTS AND DISCUSSION

## 4.1 Fiber Diameter

The diameters of fibers were measured from SEM photos by using the function of the embedded software. The averages and standard deviations were calculated from the collected 20 figures for each sample. Results were plotted to find the dependency of voltage and concentration. Generally, they followed the expected tendency in Figure 5 that fibers would get thinner when voltage increased, and thicker when solute (PVP and SOG) concentration increased.

### 4.1.1 Influence of Voltage

There are two plots available here, describing the relationship between diameter and voltage. In the first plot, the precursor concentration is 100% mixed with different polymer concentration; in the second plot, the polymer solution is 0.04 g/mL with different precursor volume concentration. Both plots have voltages ranging from 3 kV to 7 kV. Average values of the diameter are expressed as diamonds, triangles, and stars. Upper limits and lower limits of standard deviation of the diameter are also expressed outside the average. SEM photos are shown after each plot. (Figure 9-12, Figure 13-16) The reason of the relationship can be explained that, when the voltage increases, there are more positive charges injected into the liquid, causing more charge repulsion inside the liquid. The polymer entanglement among the polymer chains inside the viscous liquid prevents it from breaking into small droplets. Therefore it stretches and makes the

volume thinner and longer, achieving a new steady state. (Figure 17) The deviation of the diameter tends to be larger when the average of diameter is larger. Based on the observation, it is probably because some silica fibers were merged together during the baking step and cannot reflect the original results right after electrospinning. The measured diameters were probably the sum of the diameters of two fibers. For the lowest-concentration solution, the fibers were around 50-80 nm thick with small deviation, and there is not much difference with increased voltage.

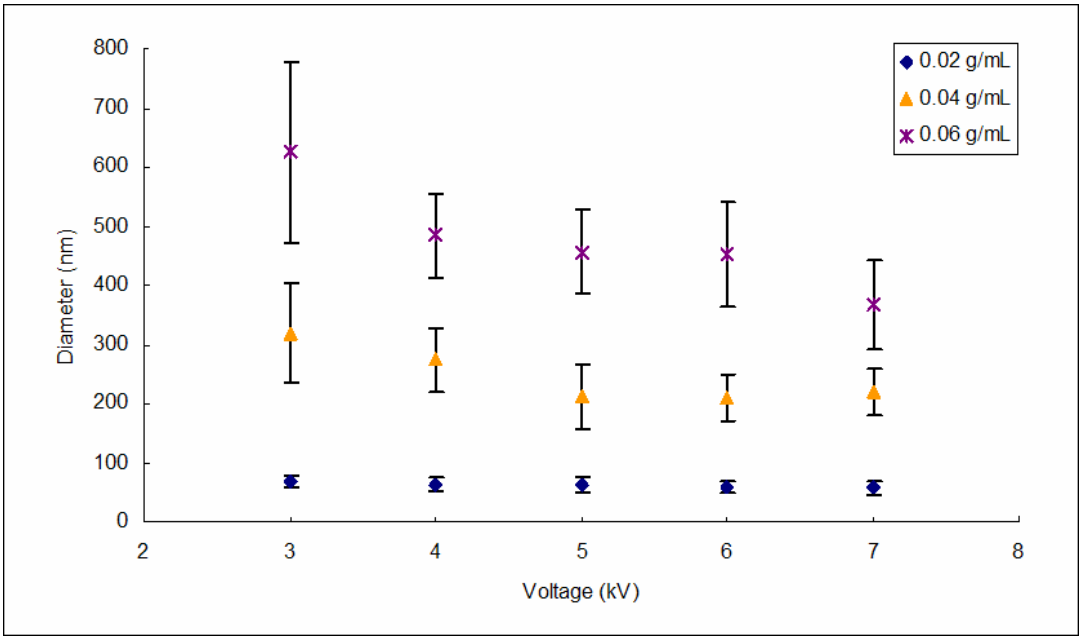


Figure 9. Nanofiber diameters as a function of voltage for different polymer (PVP) concentration.

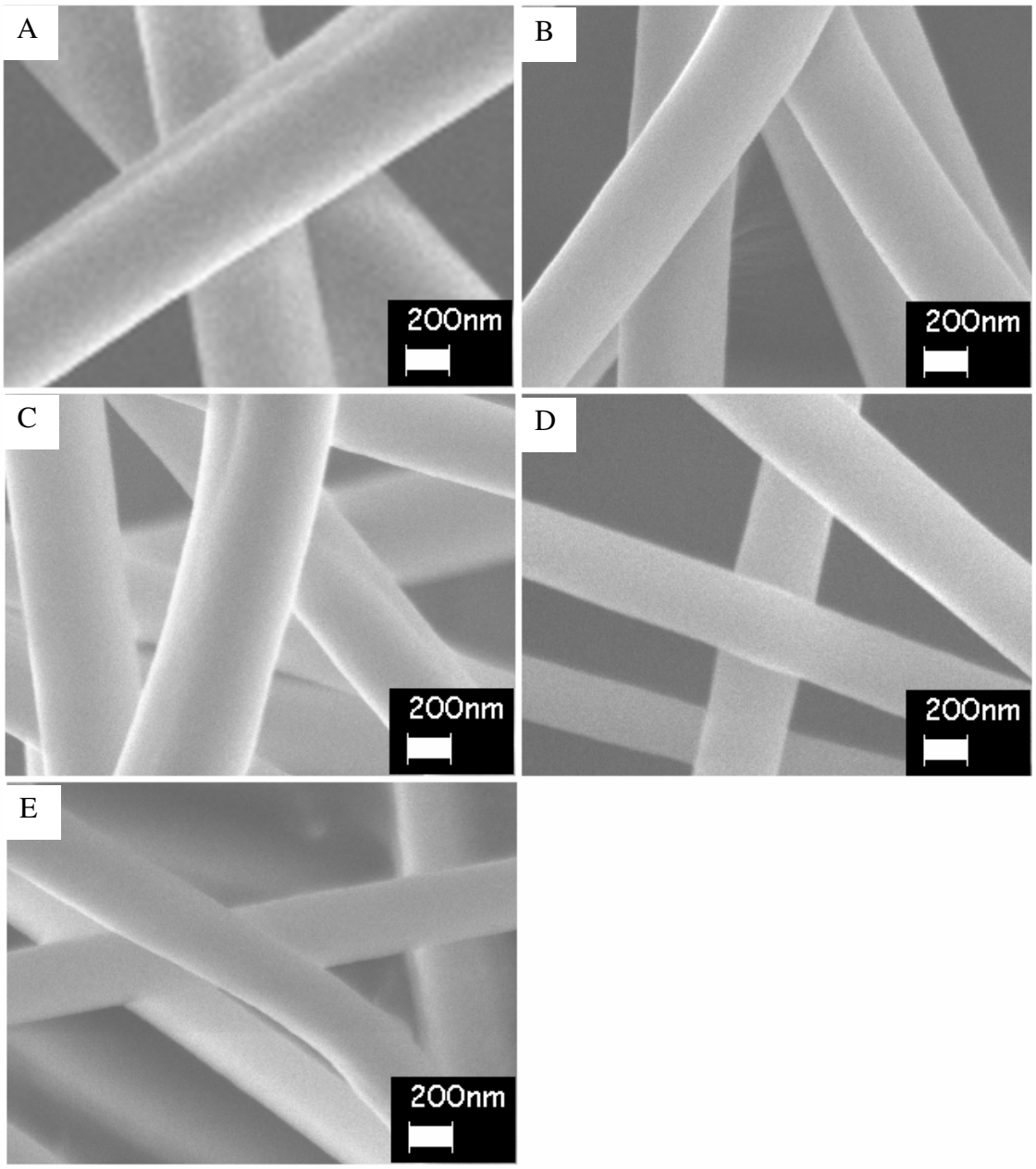


Figure 10. SEM photos of silica fibers spun from 0.06 g/mL PVP concentration at different voltages. (A) 3 kV; (B) 4 kV; (C) 5 kV; (D) 6 kV; (E) 7 kV.

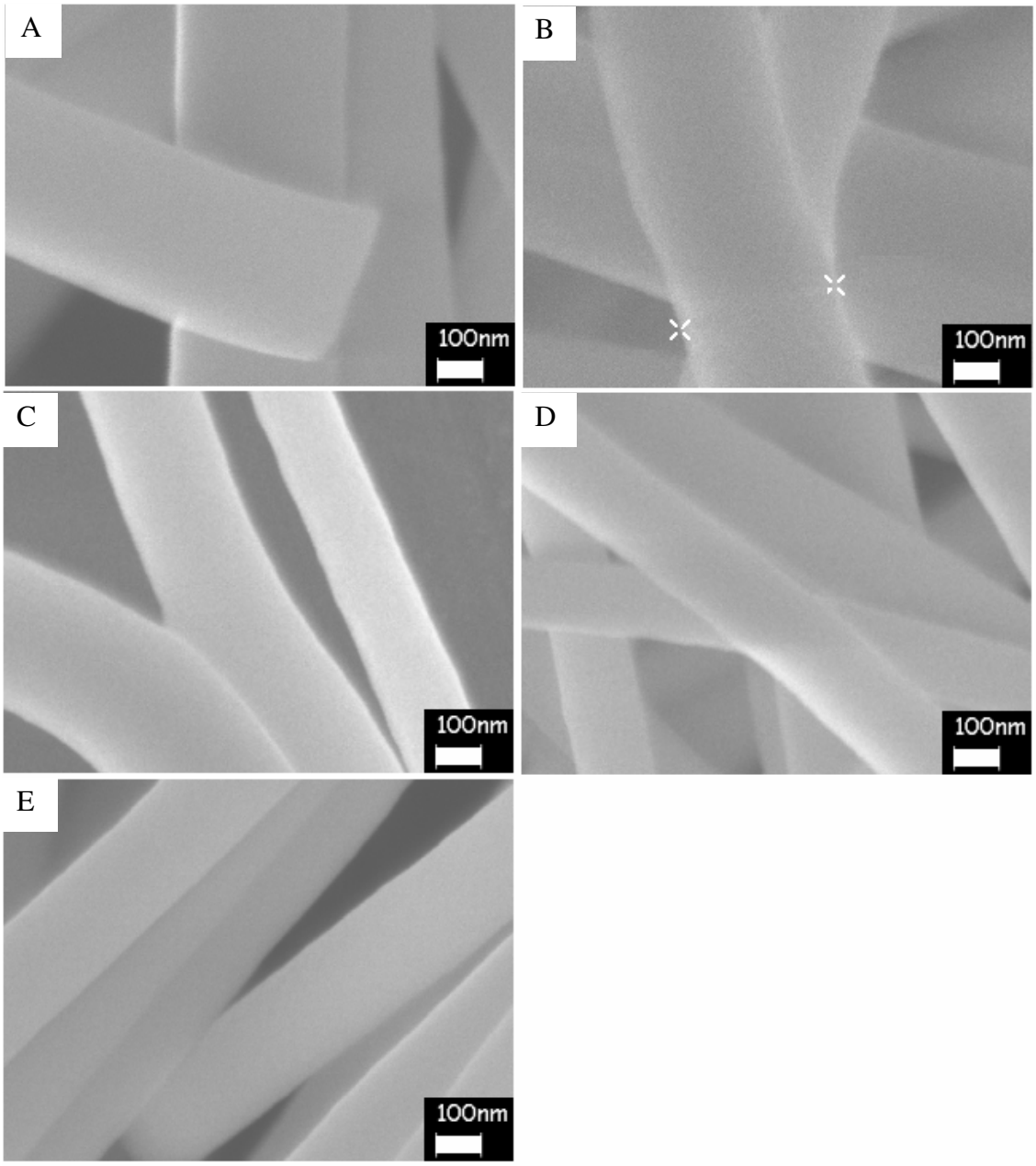


Figure 11. SEM photos of silica fibers spun from 0.04 g/mL PVP concentration at different voltages. (A) 3 kV; (B) 4 kV; (C) 5 kV; (D) 6 kV; (E) 7 kV.

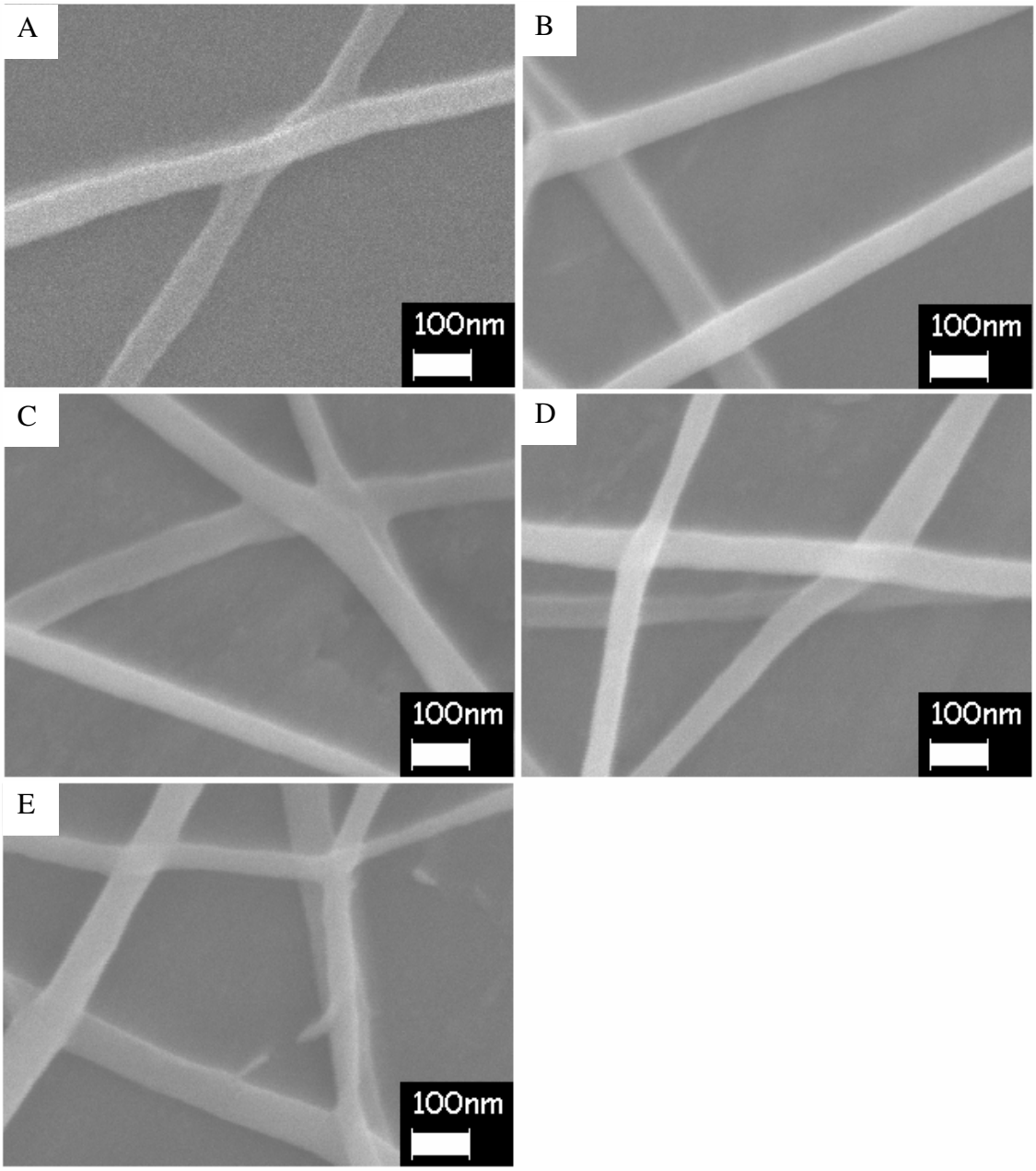


Figure 12. SEM photos of silica fibers spun from 0.02 g/mL PVP concentration at different voltages. (A) 3 kV; (B) 4 kV; (C) 5 kV; (D) 6 kV; (E) 7 kV.

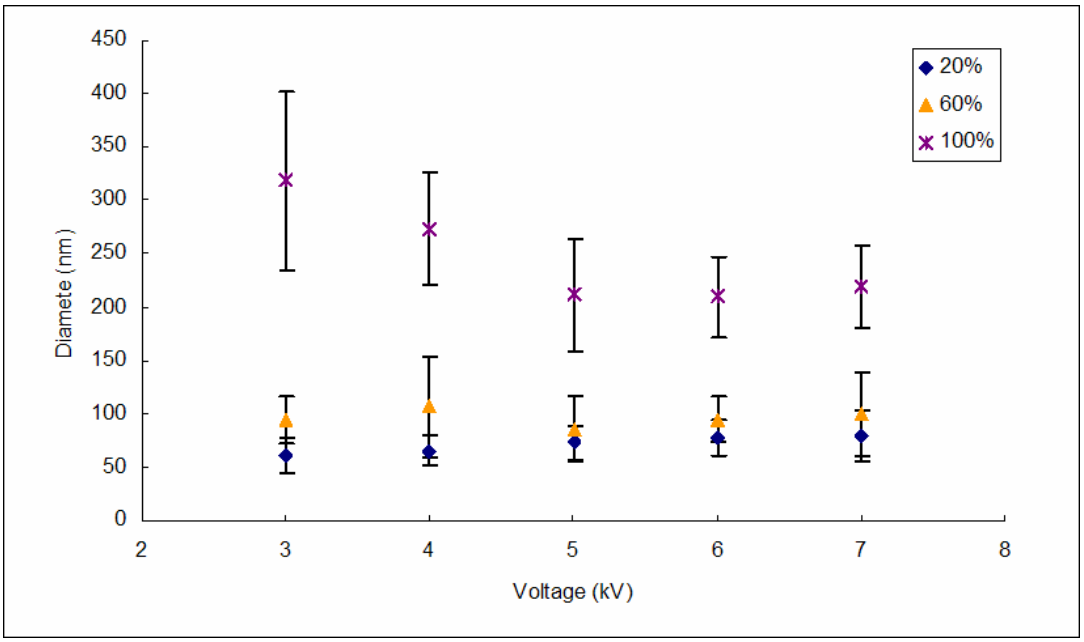


Figure 13. Nanofiber diameters as a function of voltage for different precursor (SOG) concentration.

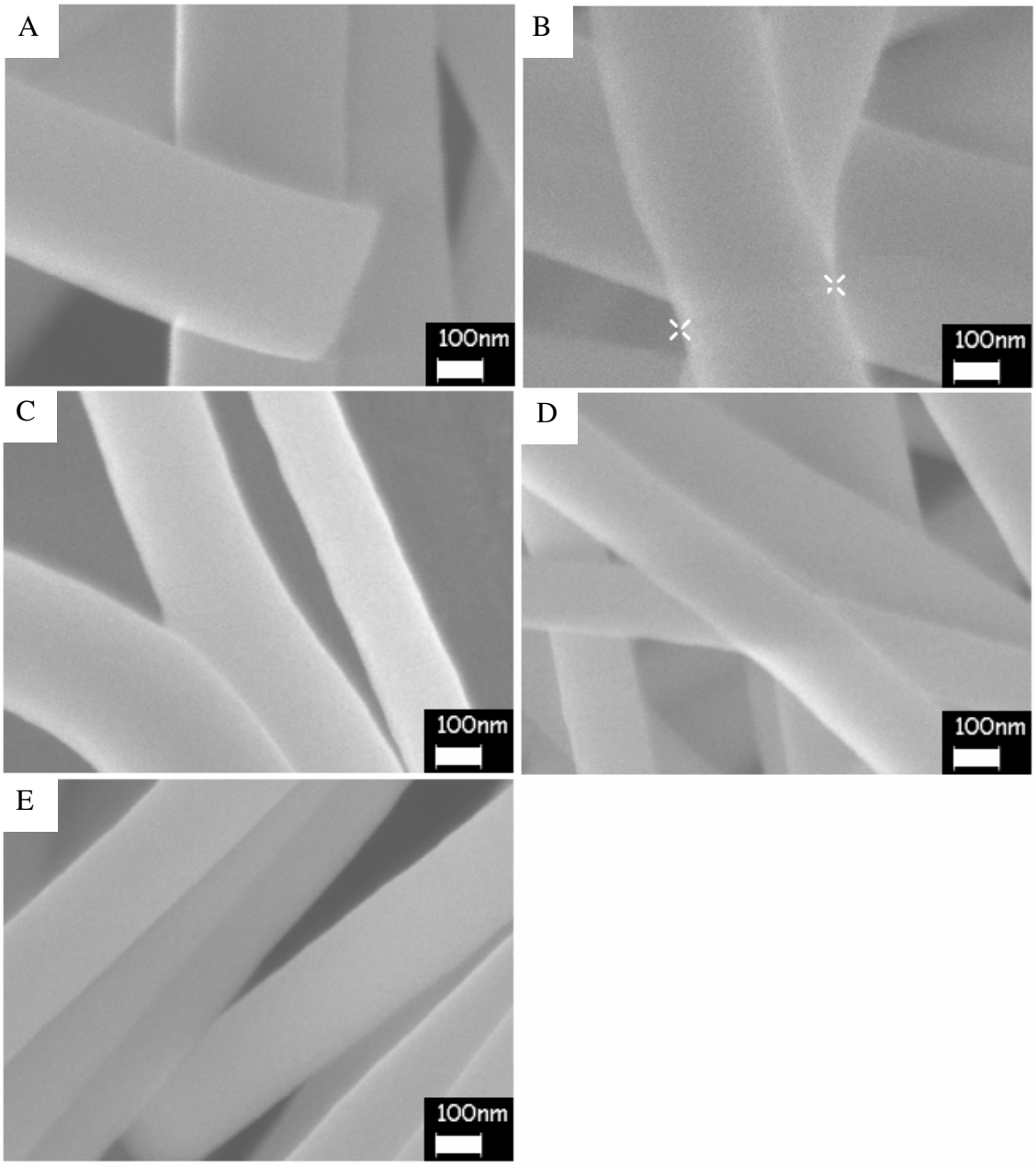


Figure 14. SEM photos of silica fibers spun from 100% SOG concentration at different voltages. (A) 3 kV; (B) 4 kV; (C) 5 kV; (D) 6 kV; (E) 7 kV.

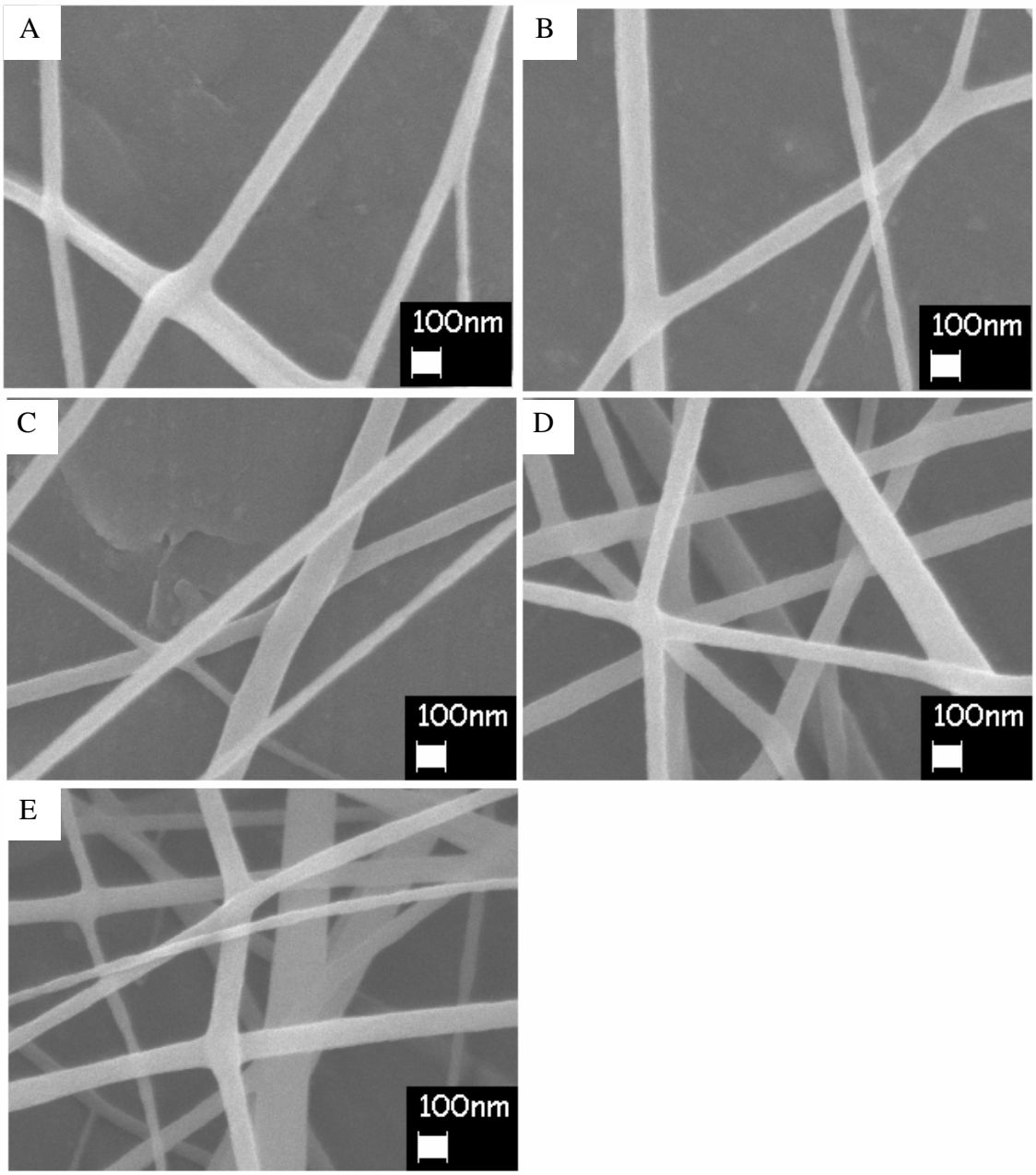


Figure 15. SEM photos of silica fibers spun from 60% SOG concentration at different voltages. (A) 3 kV; (B) 4 kV; (C) 5 kV; (D) 6 kV; (E) 7 kV.

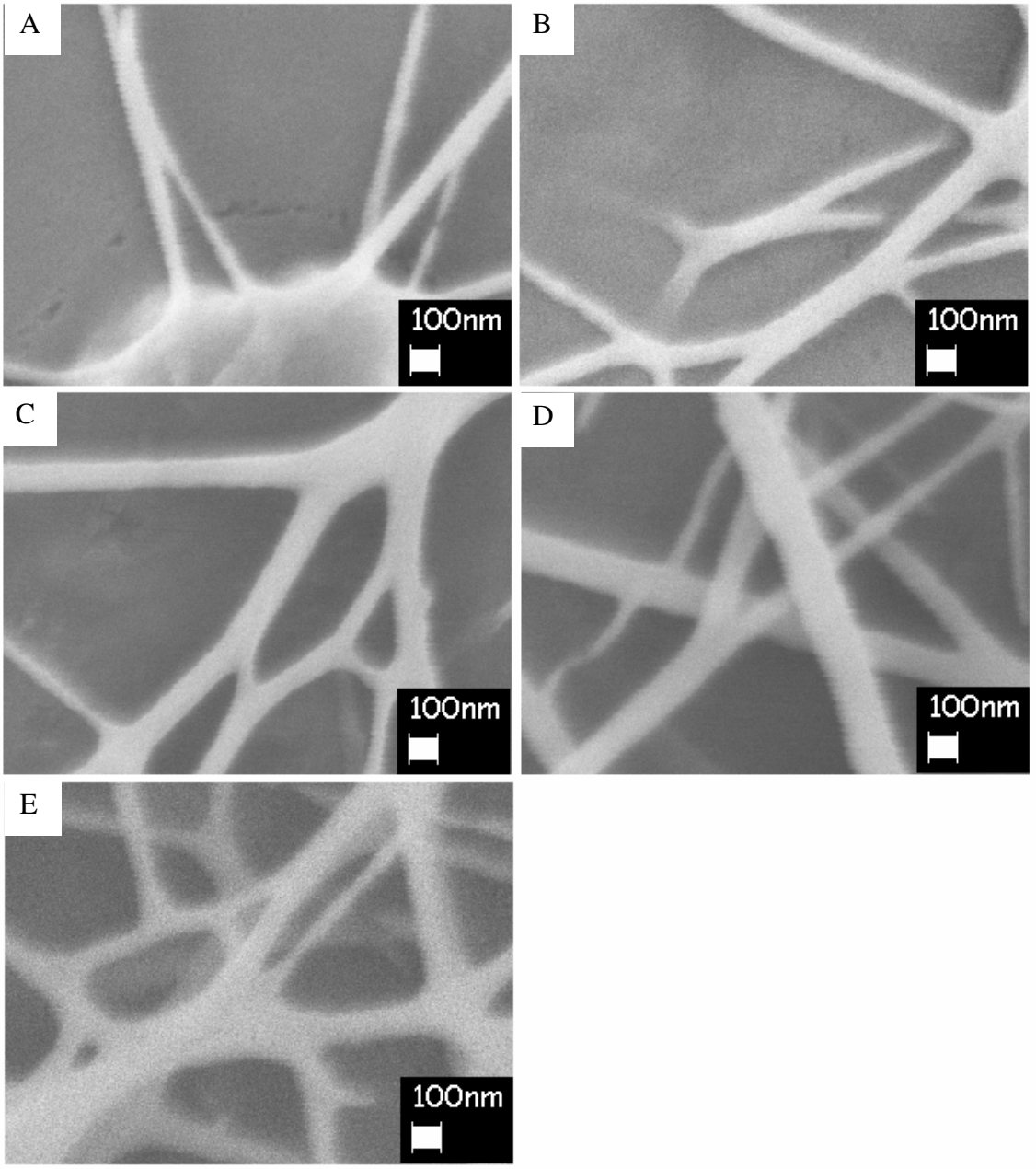


Figure 16. SEM photos of silica fibers spun from 20% SOG concentration at different voltages. (A) 3 kV; (B) 4 kV; (C) 5 kV; (D) 6 kV; (E) 7 kV.

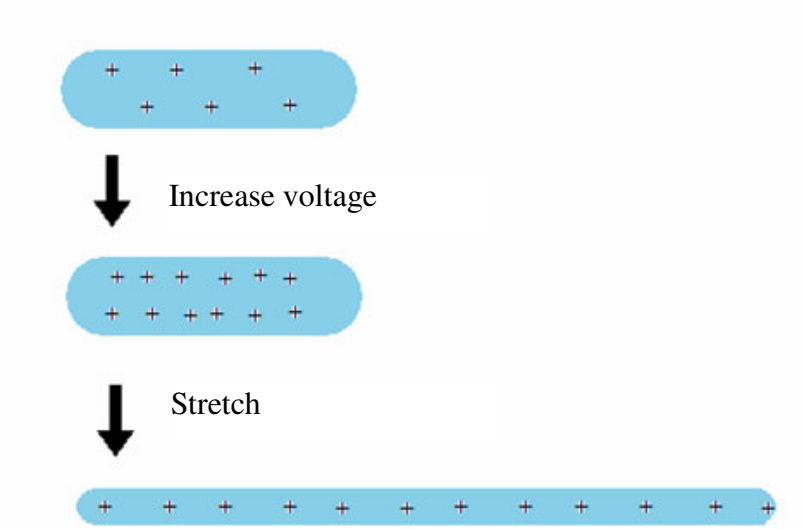


Figure 17. The explanation of the voltage-dependent results. The liquid stretches and shrinks due to the viscosity and increased voltage.

4.1.2 Influence of Polymer Concentration

The results are shown in SEM photos in Figure 18 (spun at 6 kV) and the plot in Figure 19. Minimum average diameter can reach 58 nm at 7 kV with standard deviation 12 nm. The diameter of fibers increases as the polymer concentration increases under the same electric field. This can be explained that, when the concentration increases, the polymer chains inside the liquid have more possibilities to entangle with each other, which causes additional resistance for the liquid to be stretched. Therefore, the electrospun composite fibers spun from high concentration are thicker than which spun from low concentration. They directly affect the resultant silica fibers. (Figure 20)

The plot does not present the whole data, because the overlap of deviation lines may cause confusion. The complete data are shown in Table 2.

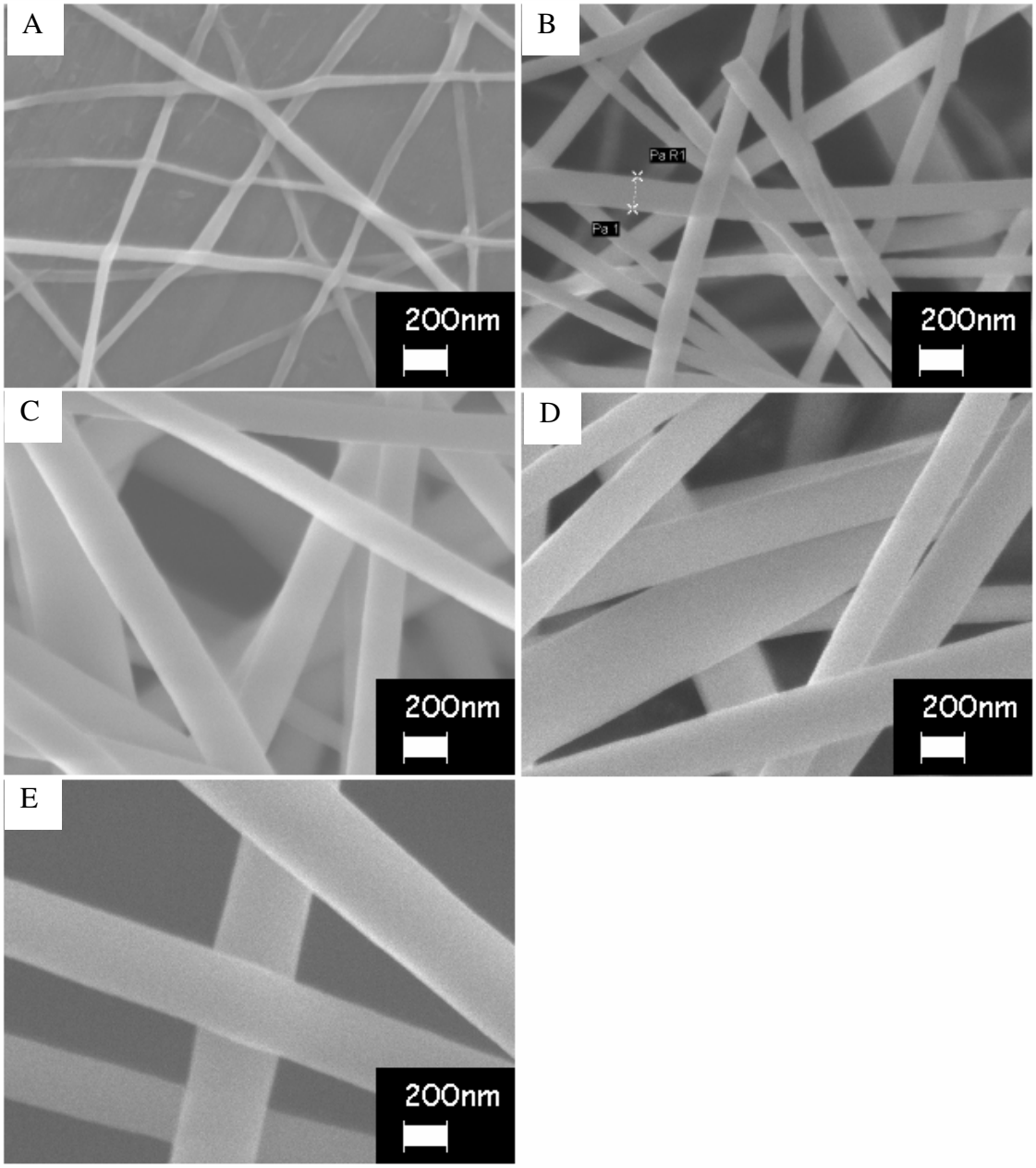


Figure 18. SEM photos of silica fibers spun from different PVP concentrations at 6 kV. (A) 0.02 g/mL; (B) 0.03 g/mL; (C) 0.04 g/mL; (D) 0.05 g/mL; (E) 0.06 g/mL.

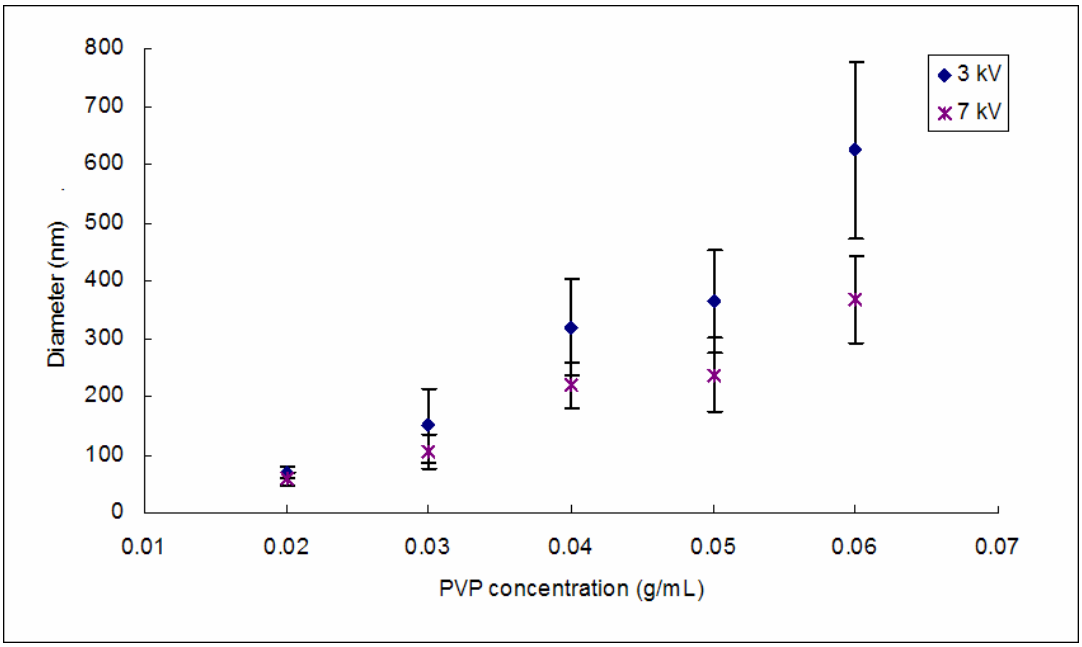


Figure 19. Nanofiber diameters as a function of PVP concentration.

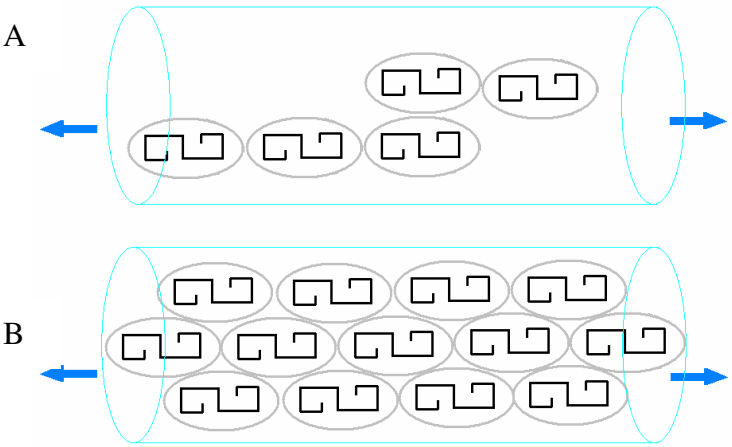


Figure 20. The schematic diagram of polymer extrusion. The fiber in (A) was electrospun from low polymer concentration solution, and had fewer chain entanglements, when compared to (B).

Table 2. The complete data of diameter-voltage-concentration relationship.

| Average (nm) | 3 kV | 4 kV | 5 kV | 6 kV | 7 kV |
|---|---|---|---|---|---|
| 0.02 g/mL | 68 | 63 | 62 | 59 | 58 |
| 0.03 g/mL | 149 | 125 | 117 | 115 | 104 |
| 0.04 g/mL | 319 | 274 | 212 | 209 | 220 |
| 0.05 g/mL | 364 | 312 | 285 | 270 | 238 |
| 0.06 g/mL | 625 | 484 | 456 | 453 | 368 |
| Deviation (nm) | | | | | |
| 0.02g/mL | 10 | 11 | 14 | 9 | 12 |
| 0.03g/mL | 65 | 47 | 53 | 24 | 30 |
| 0.04g/mL | 84 | 53 | 53 | 38 | 38 |
| 0.05g/mL | 88 | 61 | 47 | 54 | 64 |
| 0.06g/mL | 152 | 71 | 70 | 89 | 75 |

### 4.1.3 Influence of Precursor Concentration

The results appear similar tendency to polymer-dependent result. The silica fibers spun at 6 kV are shown in Figure 21, and the relationship are plotted in Figure 22. Minimum average of diameter was 58 nm and happened at 7 kV with 40% precursor volume concentration. The diameter generally increases as the volume concentration increases. It can be explained by Figure 23. When more silica precursors exist in fibers, more silica parts remain in fibers after the baking process. Therefore, the resultant fibers are thicker.

The plot does not present the whole data either, and the complete data are shown in Table 3. There are two interesting results. First, the minimum average of diameter does not happen in 20%. It is conjectured that the precursor concentration was too low, causing the uneven distribution of precursor inside the composite spun fibers. The silica parts aggregated in parts after baking, which resulted in fibers thicker than those spun from 40%. (Figure 24) In addition, there is a gap between the results of 100% precursor volume concentration and those of 80% or less. Compared to the 20-40% solution, it is recommended to use 60%-80% solution to achieve 100 nm silica fibers, since more silica fibers will remain after the baking at the same time.

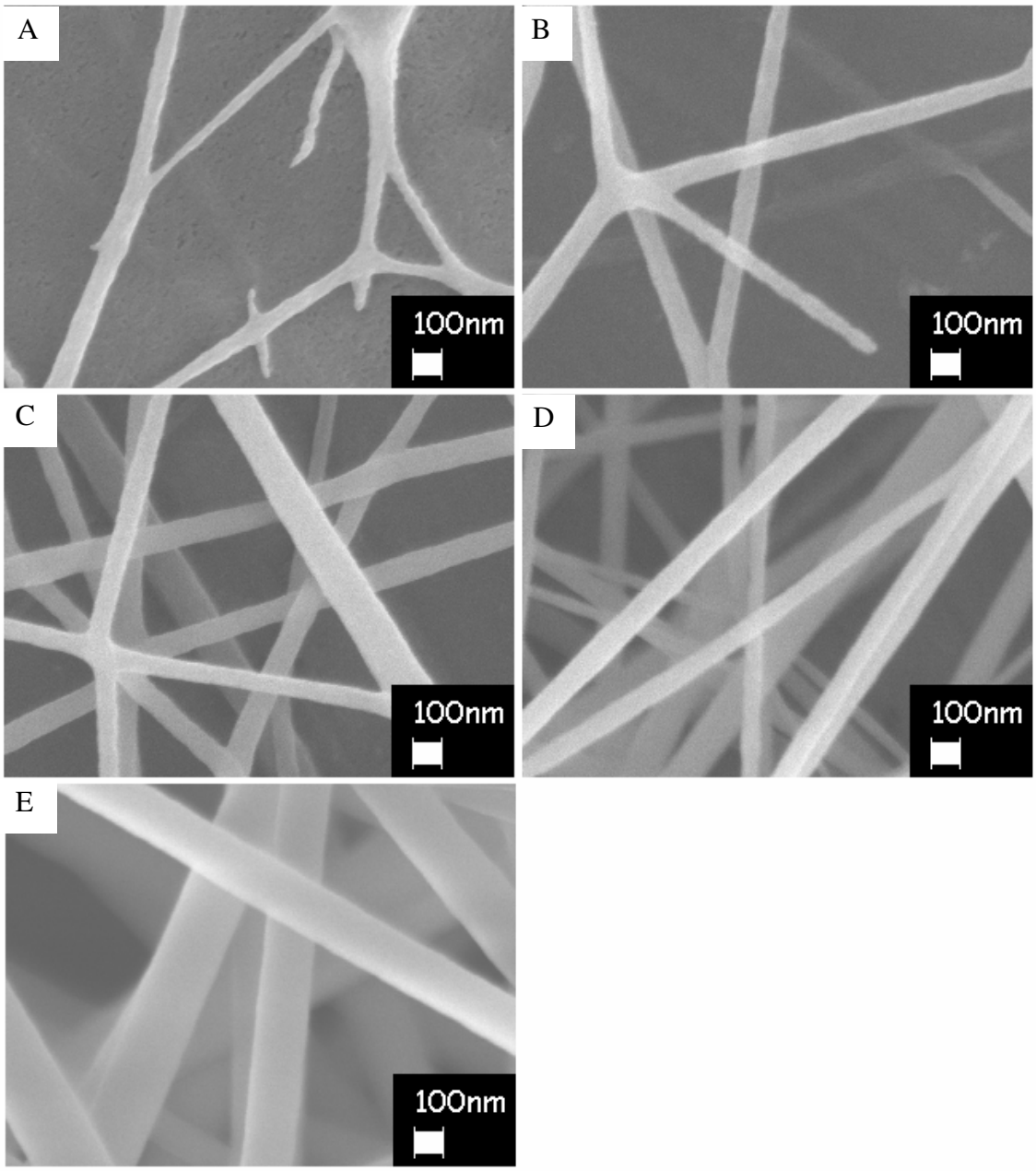


Figure 21. SEM photos of silica fibers spun from different SOG concentrations at 6 kV. (A) 0.02 g/mL; (B) 0.03 g/mL; (C) 0.04 g/mL; (D) 0.05 g/mL; (E) 0.06 g/mL.

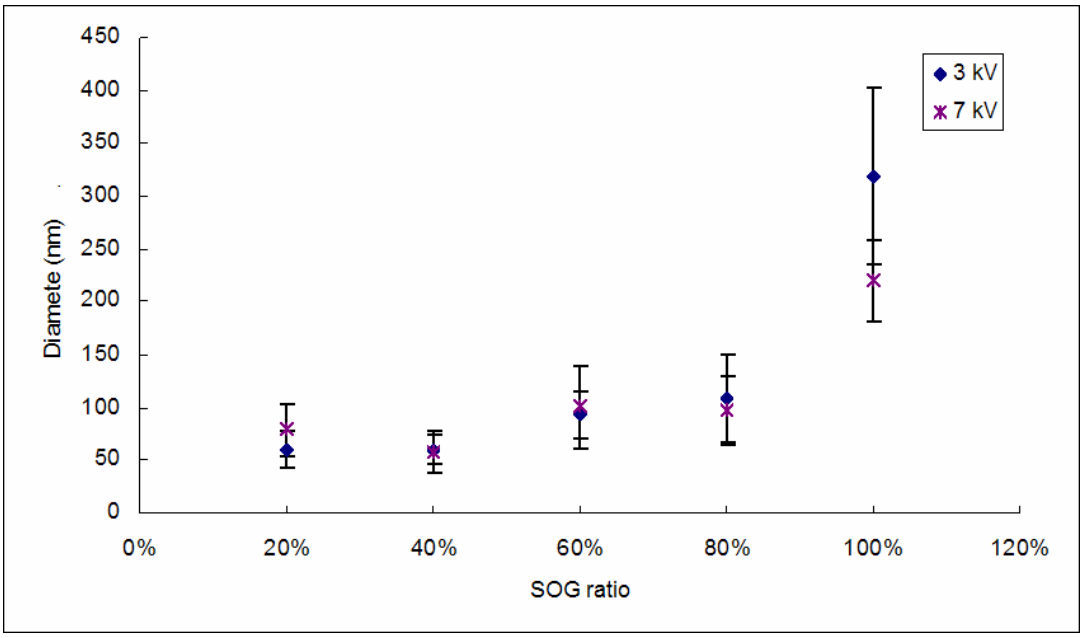


Figure 22. Nanofiber diameters as a function of SOG concentration.

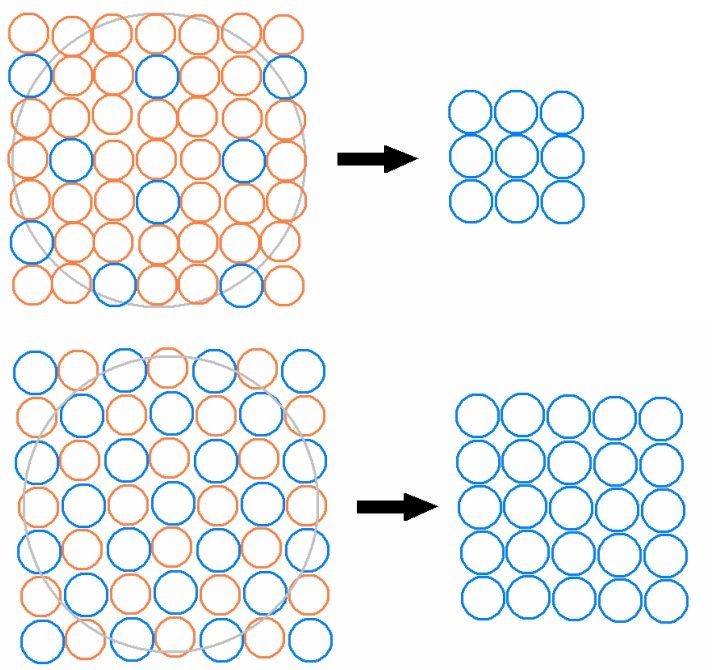

Figure 23. The schematic diagram of precursor influence. Blue circle and orange circle represent silica precursor and polymer parts. More silica remain in baked fibers if they are spun from higher precursor concentration, which means the fibers will be thicker.

Table 3. The complete data of diameter-voltage-volume ratio relationship.

| Average (nm) | 3 kV | 4 kV | 5 kV | 6 kV | 7 kV |
|---|---|---|---|---|---|
| 20% | 61 | 65 | 73 | 77 | 79 |
| 40% | 60 | 64 | 68 | 60 | 58 |
| 60% | 94 | 107 | 85 | 94 | 100 |
| 80% | 108 | 107 | 115 | 93 | 98 |
| 100% | 319 | 274 | 212 | 209 | 220 |
| Deviation (nm) | | | | | |
| 20% | 16 | 14 | 16 | 17 | 24 |
| 40% | 14 | 13 | 26 | 20 | 19 |
| 60% | 23 | 47 | 30 | 21 | 39 |
| 80% | 42 | 31 | 22 | 28 | 33 |
| 100% | 84 | 53 | 53 | 38 | 38 |

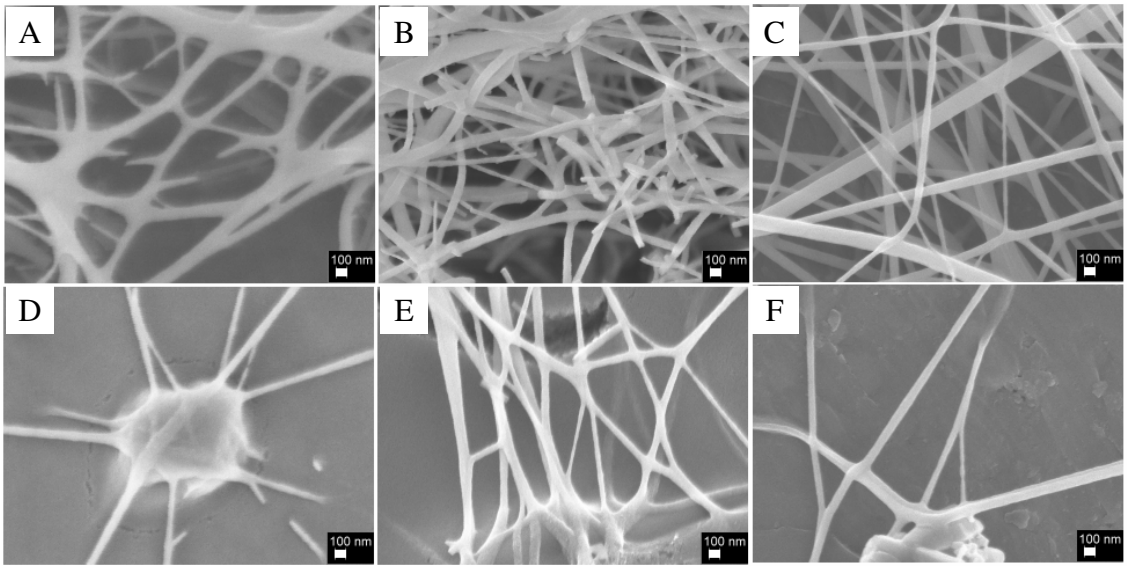


Figure 24. SEM photos of silica fibers electrospun from low precursor concentration. (A) to (C): fibers spun at 7 kV with 20%, 40%, and 60 % of precursor volume concentration; (D) to (F): 3 kV with 20%, 40%, and 60 % of precursor volume concentration. The scale bars are 100 nm.

## 4.2 Pore Size

The experiment was performed by using 80% precursor volume concentration and 0.04 g/mL PVP solution. The spun time was from 1 to 5 minutes. The pore sizes were recorded by estimating the diameter inside a pore area, which were defined in the experimental section. The averages and standard deviations were calculated from the collected 10 figures for each sample. SEM photos, the relationship plot are shown in Figure 25 and Figure 26, and the results show that time factor does not influence the pore sizes. At first glance, it sounds strange that longer electrospun time dose not affect the results, since the overlap of fibers should make the pore size smaller. However, the method used here cannot measure the permeability of the membrane or transportation properties mentioned in previous studies,[5] but can only estimate the size within a few layers. It leads to a conclusion that fibers were deposited at the same rate, and were randomly distributed.

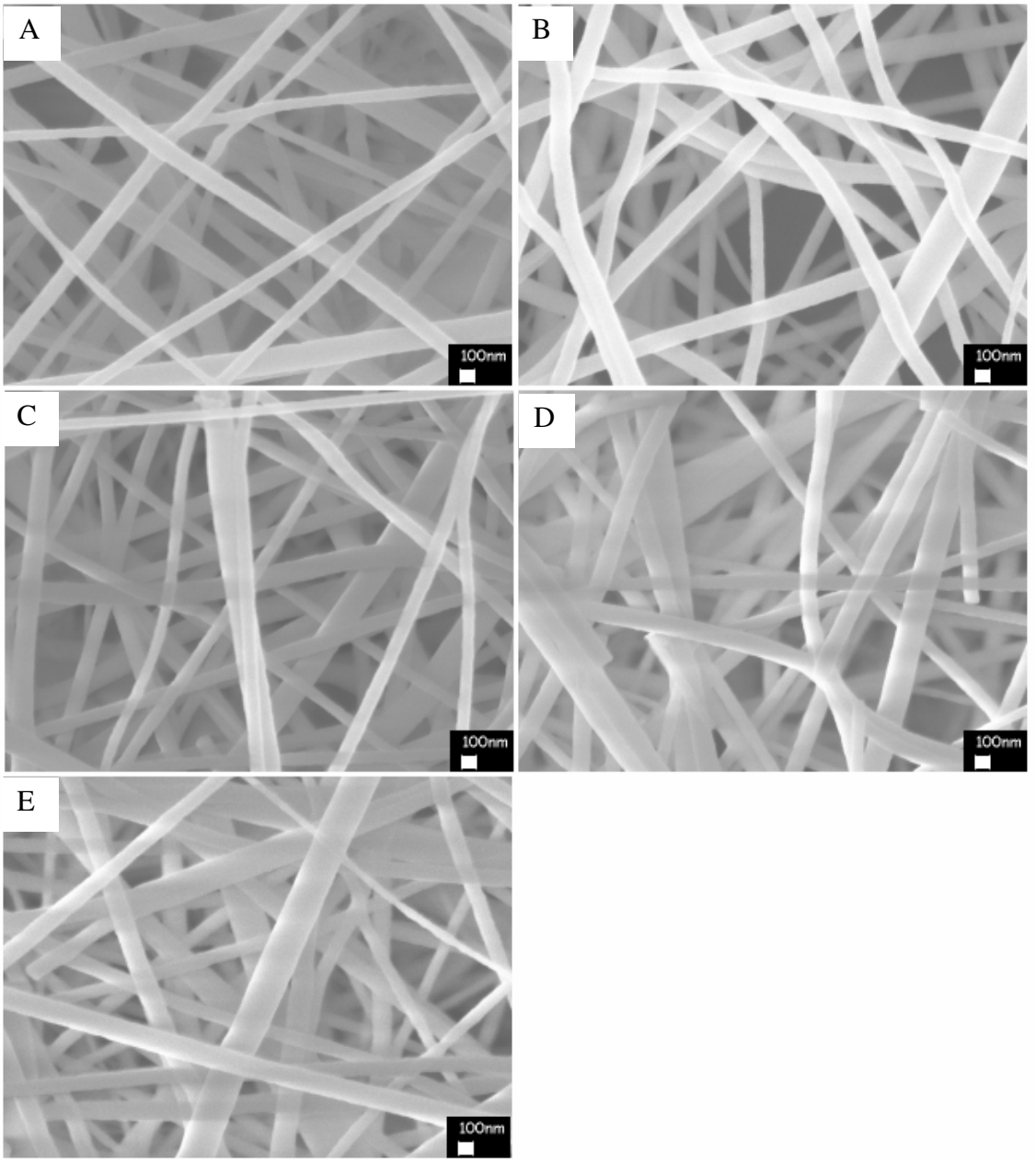


Figure 25. SEM photos of silica fibers spun from 80% SOG and 0.04 g/mL PVP at 6 kV. (A) 1 minute; (B) 2 minutes; (C) 3 minutes; (D) 4 minutes; (E) 5 minutes. The scale bars are 100 nm.

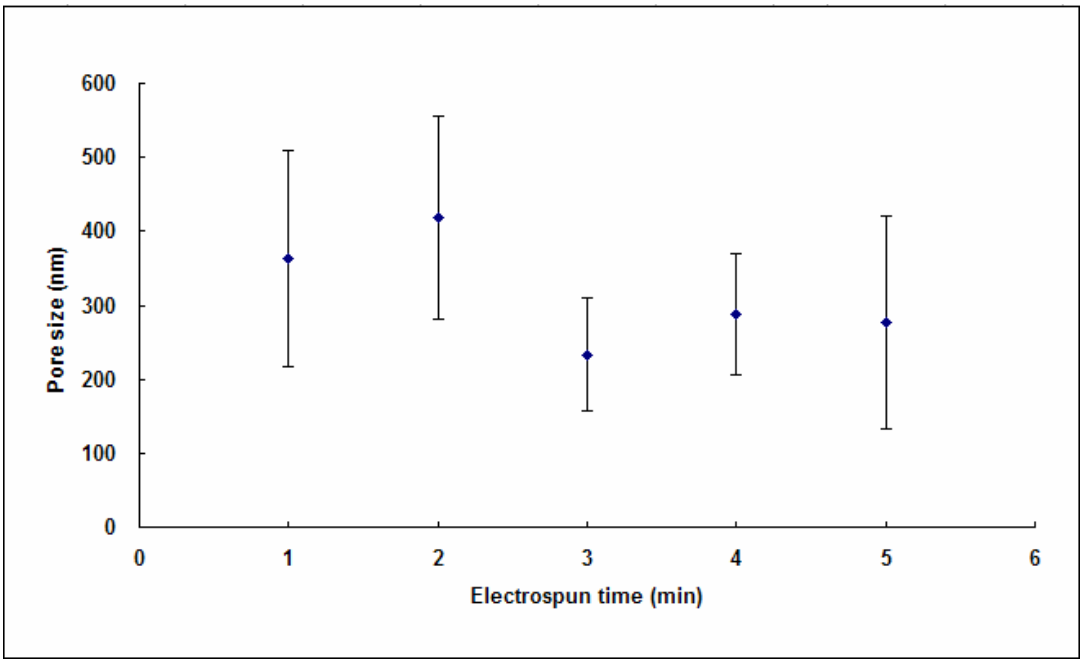


Figure 26. The pore size-time relationship.

## 4.3 Hybridization Test

The signals were recorded by X-ray films shown in Figure 27. The darker area indicated more photon signals were received. As expected, the fiber membrane that coated with protein B had the strongest signal when the exposure time was 10 seconds (short exposure). The other membrane did not have signal because the secondary antibodies could not bind to the protein A, therefore no enzymes were bound. The other slide showed no signal in short exposure since most protein B were washed away. However, for long exposure (2 minutes), signal can be detected, showing that still a few protein B remained on it. The RGB (Red, Green, and Blue) values of the signalled area in the photos are calculated. Value 255 represents white and value 0 represents black. The small rectangular area in membrane B is used as the defined region to measure the value. For short exposure, membrane B has the average value of 86 and glass slide B has the value 219. For long exposure, membrane B has the average value 34 and glass slide B has the value 200. The estimated light absorption is therefore 60.73% (membrane) and 0% (glass) for short exposure, and 84.47% (membrane) and 8.68% (glass) for long exposure. In brief, the results implie that fiber membranes can be used as the platform for the reaction of antigens and antibodies.

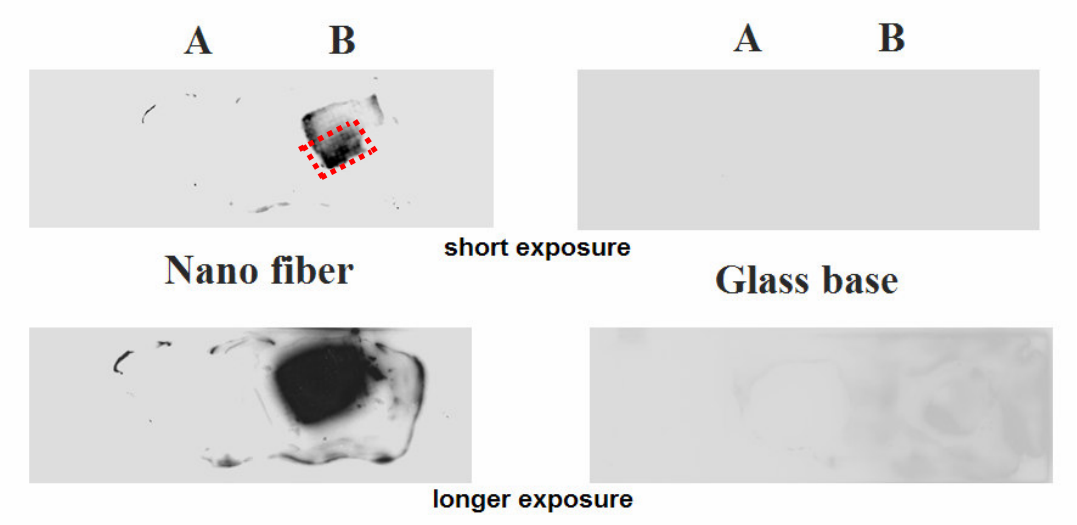


Figure 27. The result of hybridization test. RGB values are measured by using a defined area shown in membrane B (dotted rectangle) for short exposure.

# 5. CONCLUSIONS

In this thesis, silica fibers were produced from electrospinning and post-baking process. The relation between diameter and parameters such as voltage, polymer concentration, and precursor concentration were studied, and the tendency fitted the expected results in most cases. The variation of fiber diameter is large for thicker fibers. It can be reduced by carefully recognize single fiber and further control the environmental factors. The characterization plots provide a useful reference for future experiments. For example, in case people need to fabricate fibers less than 100 nm in diameter, they can use solution made of PVP 0.04 g/mL and SOG 80% or made of PVP 0.02 g/mL and SOG 100%., and electrospin under the parameters mentioned before. By switching the voltage back and forth from 3 kV to 7 kV, it is possible to deposit fibers having different size layer by layer.

The fiber membranes performed well in the hybridization test. The filter-like structure of fiber membranes can catch more bio-molecules such as antigens or antibodies than the smooth surface of glass slides after washing. They have stronger attraction for proteins due to their extremely high surface areas, which can much increase the exposure to molecules. It shows potential application in molecular detection. Based on the idea, the ELISA plates can be improved by replacing the plastic well with filter membrane, so that the molecules can pass through and stay in the membranes. A possible device is shown in Figure 28. Several small pieces of membranes can be sandwiched by two perforated boards. Samples are injected through each pore by using

syringes or pipettes. Each small piece acts like an ELISA well. The pore size is 1 mm in diameter, so only very small amount of sample is needed. It is expected that this new device will have very high sensitivity in molecular detection even for very low concentration samples.

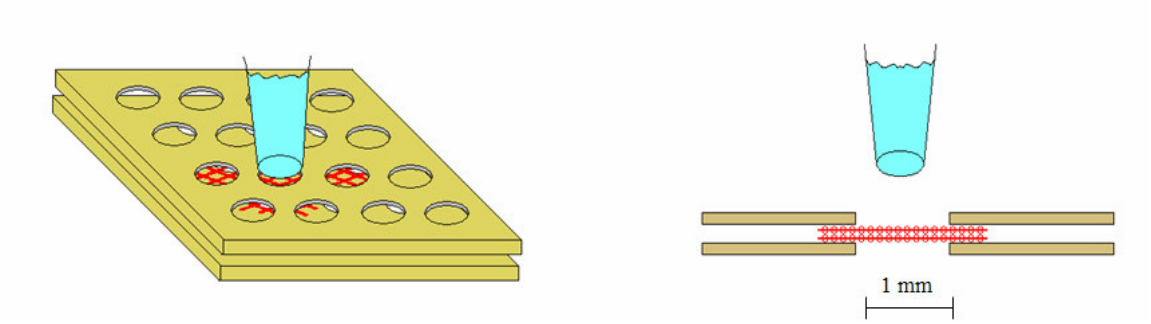


Figure 28. The new detection device integrating electrospun nanofiber membranes.

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