Synthesis and gas sensing property of electrospun titanium dioxide microfiber for the application of personal protective equipment

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**SYNTHESIS AND GAS SENSING PROPERTY OF
ELECTROSPUN TITANIUM DIOXIDE MICROFIBER
FOR THE APPLICATION OF
PERSONAL PROTECTIVE EQUIPMENT**

THANIT APIWATTANADEJ

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2020

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PERSONAL PROTECTIVE EQUIPMENT**

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School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Master of Engineering

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Thanit Apiwattanadej

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Thanit Apiwattanadej

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Abstract

Gas sensing microfiber is one of the most challenging electronic textile components, whose development is hindered by limitations of gas sensing materials, including the brittleness of metal oxides and the slow response of chemiresistive polymers. Hence, current trend on the microfiber gas sensor is moving toward the composite microfiber fabrication. In this report, the basis for the fabrication and the characterization of gas sensing microfiber are established.

To initiate the study, titanium dioxide (TiO_2), which is a common chemiresistive metal oxide, has been used as a model sensing material for the gas sensing microfiber fabrication owing to its high sensitivity, fast response and low cost. The fabrication of TiO_2 microfiber membrane begins with the electrospinning of titanium nitride nanoparticles in polyvinylpyrrolidone (TiN-NPs/PVP). The composite microfiber membranes are subsequently heated in the furnace to burn away PVP substrate and oxidize TiN to TiO_2 . The electrospinning parameters are optimized to produce mesoporous TiO_2 microfiber membrane with fiber diameter in the range of 200 – 700 nm. The x-ray diffraction results show that the crystallite structures of TiO_2 microfiber are controllable by the annealing temperature. The anatase phase tends to dominate in TiO_2 microfiber at the curing temperature of 500°C , while rutile phase is dominant at the curing temperature of 700°C . The carbon monoxide (CO) gas sensing properties of mesoporous TiO_2 microfiber membrane with rutile phase dominant are investigated using custom-design gas sensor characterization system. The resistance of mesoporous TiO_2 microfiber membrane decreases from $6.40\text{ G}\Omega$ to $3.86\text{ G}\Omega$ upon exposing to CO gas concentration of 200 ppm at 350°C . The response and the recovery time of the sample are 120 seconds and 102 seconds respectively. The subsequent study on mesoporous TiO_2 microfiber membrane will focus on the optimum working temperature and the improvement of the sensitivity and the selectivity of the sensor.

The understanding in both electrospinning process and gas sensor characterization lays strong foundation for the fabrication of composite microfiber gas sensors. Subsequent studies on chemiresistive polymer microfibers and the fabrication of flexible gas sensors have been planned to achieve high-performance gas sensors for personal protective equipment.

Chapter 1

Introduction

1.1 Background

Since the beginning of 20th century, electronic devices have been significantly transformed from bulky computer workstations to portable devices because of the microfabrication technology [1-3]. Besides miniaturization, several researchers further attempted to develop flexible and stretchable electronic circuitry for wearable electronic devices using serpentine or curve interconnection patterns on flexible polymers, such as, polydimethylsiloxane (PDMS), parylene, and polyurethane [4-7]. Nevertheless, the applications of wearable devices are still limited because of poor air and moisture ventilation of polymer substrates. Therefore, breathability has become the new requirement for flexible electronic devices lately [8-11].

Instead of using conventional polymers for flexible electronics, textiles are promising candidates for wearable electronic devices because of their excellent wearability and air permeability [12-14]. The integration of electronic devices and textiles is typically called, “electronic textile (E-textile)” [15] or “electronic broidery (E-broidery)”[16]. Several conceptual designs of E-textile have been realized by the collaboration between researchers and designers since 2000s [17]. Metals or metal oxides are usually deposited on fibers using deposition techniques such as sputtering, chemical vapor deposition (CVD), physical vapor deposition (PVD), electrodeposition and screen-printing [18]. Then the hydrophobic polymers such as polyurethane and silicone are coated to protect the deposited materials [19].

Although these surface modification techniques seem to be straightforward, multilayer fibers are incompatible with textile manufacturing process because of poor tensile strength, low percent of elongation and inflexibility [20-22]. These mechanical limitations lead to active research on direct fabrication of electronic fiber from metals [23], semiconductors [24, 25],

carbon nanostructures, and conductive polymers [26].

Among spinning techniques, electrospinning is suitable for nano/microfiber research owing to its simplicity, versatility, and low-cost [27]. Fundamentally, electrospinning produces fibers by ejecting polymer/composite solution through the die under the influence of high electric field. The produced non-woven membrane, and one-dimensional materials are appealing for high-performance filters, and ultrasensitive sensors [28, 29].

One of the potential applications of the electrospun microfibers is high-performance gas sensing microfibers for personal protective equipment (PPE) [30-32]. The traditional chemical gas sensor fibers required metal oxides, such as tin dioxide (SnO_2) and titanium dioxide (TiO_2), for high sensitivity and fast response [28, 29]; however, brittleness of metal oxide materials is not compatible with textile manufacturing. Alternatively, stretchable conductive polymers, such as polypyrrole (PPy) or polyaniline (PANI) [33-35], and carbon nanostructures including carbon nanotube and graphene [36-38], are promising materials for gas sensing microfibers. The disadvantages of these materials are poor stability and slow response of conductive polymers [25].

As a result, the current trend of microfiber gas sensors for E-textile is moving toward composite fibers to combine flexibility and stretchability of conductive polymer with high sensitivity of metal oxide materials [39, 40]. In this research, the fabrication of TiO_2 microfiber membrane using the electrospinning of titanium nitride nanoparticles in polyvinylpyrrolidone (TiN-NPs/PVP) is studied. The understanding on metal oxide electrospinning, material characterization and gas characterization will be the fundamental knowledge for gas sensing composite microfiber fabrication in the next phase.

1.2 Objectives

This research project aims to produce electrospun microfibers for the high-performance gas sensors. The successful gas sensing microfiber fabrication and characterization will be the basis for flexible gas sensing microfiber development.

1.3 Scope of the work

The detailed scope of work to achieve the objective can be categorized into the following areas:

1. Titanium dioxide (TiO_2) microfiber membrane is fabricated by colloidal electrospinning approach. The morphology and the crystallinity of TiO_2 nanofibers are characterized by using field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and energy dispersive X-ray (EDX).
2. The gas-sensing behavior of the fabricated microfiber membrane is evaluated by using carbon monoxide (CO) as the model hazardous gas in the controlled gas chamber. The primary evaluation parameters include sensitivity, response time and recovery time.
3. The microfibers are deposited on either interdigitated electrode (IDE) or integrated with conductive fabric to demonstrate the application in personal protective equipment (PPE).

1.4 Outline of the report

Chapter 1 gives a brief introduction to the status of E-textiles, leading to the motivation of producing high-performance gas sensing microfibers. Objective and scope of the research are discussed. Chapter 2 reviews the current E-textiles technologies and the colloidal electrospinning. Chapter 3 describes the research methodology for the TiO_2 microfibers fabrications, the characterization methods and the gas sensing performance evaluations while Chapter 4 presents the results and discussions in details. Finally, Chapter 5 concludes the works done so far and proposes the future directions for this project.

Chapter 2

Literature Review

2.1 Wearable electronic device

Historically, wearable electronic devices have been evolving along with the miniaturization of electronic components since 20th century. The first generation of wearable electronic devices were assembled from multiple portable devices attached on headgear and clothing as demonstrated in Figure 1. These devices were bulky and noticeable, for example, the in-shoe cigarette size device for roulette prediction and the head-mounted wearable computer for augmented reality [1, 2]. Nowadays, wearable device industry is driven from three leading segments, i.e. entertainment, fitness&healthcare, and public safety [41]. As a results, several sensor modules for motion tracking and vital sign monitoring are extensively integrated into wearable electronic devices such as smartwatch [42, 43], fitness tracking bracelet [44, 45], and smartglass [46, 47].

To further improve the wearability and the comfortability for users, many researchers have attempted to develop flexible and stretchable electronic devices by depositing thin film and curve pattern of metal and semiconductor materials on plastic and elastomer substrates, such as polyethylene terephthalate (PET), polyimide (PI), and polydimethylsiloxane (PDMS) [4-7]. This breakthrough in flexible electronic fabrication led to the progress in the development of high-quality electrodes for biological signal detection including electroencephalogram (EEG), electromyogram (EMG) and electrocardiogram (ECG) [48-50]. Besides flexible electrodes, the other flexible electronic components, such as, sensors, transistors, and displays have been intensively studied lately [51, 52].

Figure 1 Timeline of wearable electronic devices and related technologies

Although flexible electronics are the promising paradigm for wearable electronic devices, their polymer substrates have low air permeability. Therefore, the state of art of wearable electronics are traditionally designed for cold environments, where the integrated flexible electronic devices are attached into sublayer of jackets, suits or coats [17]. However, such designs are not suitable in tropical area, where heat dissipation through skin perspiration is necessary. Ideally, flexible electronics should have sufficient air and water vapor ventilation to prevent the accumulation of moisture and heat on the skin surface. Hence, recent research on the flexible electronics are trying to introduce breathable properties to electronic devices [8-11].

Instead of using flexible polymers as a substrate for the flexible electronics, textiles gain attention from research society due to their wearability and excellent air permeability. This integration of electronic devices and clothing are also known as “electronic textile (E-textile)” [15, 17, 53]. Though E-textiles are still in the research and development phase, there are some

commercially available E-textile products, which utilize conductive fabric as electrodes and capacitive sensors, for example, smart shirt [54, 55], smart bras [56], smart socks [57], and interactive jacket [58]. Therefore, the value of E-textile market are predicted up to \$5 billion from the three main driving industries of entertainment, healthcare&fitness and public safety by 2027 [41, 59].

2.2 The challenges of E-textile developments

The current research and development on E-textile can be broadly divided into four areas: (1) the compatibility of textile-based electronic components with textile machinery, (2) the interconnection between E-textile and rigid electronic circuits, (3) the encapsulation of E-textiles and (4) the functionalities of fiber-based electronic components.

Figure 2 The challenges in electronic textile developments

The first research area of E-textiles is to improve the mechanical compatibility of conductive fiber with the existing textile machinery including the sewing machine and the weaving machine for mass production. Although stainless steel or silver threads are commercially available for the hobbists, the research has shown that these conductive threads cannot telorate large multi-directional stress and strain from industrial textile machinery [60]. Hences, metal fibers are usually twisted, winded, or wrapped with traditional textile fibers, e.g. cotton or polyester, to improve the durability and sewability [61, 62].

Beside the compatibility with textile manufacturing process, current e-textile products rely heavily on the embroidery of electronic components using conductive yarns on traditional fabric [16]. The contact resistance between conductive fibers and electronics components is crucial factor of the system reliability [63]. As a results, the interconnection techniques between electronic fibers and rigid electronic components become the second challenging research area of E-textile [63-65].

The third challenging topic for E-textile product development is the encapsulation method. Although the encapsulation methods for flexible electronics such as transfer molding, hot melting and hot pressing of thermoplastic polyurethane (TPU) and silicone can be applied to E-textile, water, as well as, sweat can be absorbed to textile circuitry by the capillary force between yarns [19, 65]. To solve this issue, the thicker and larger encasulated layer could be implemented; however, thick and large encapsulated layer will obstruct air and moisture permeability, which are the main benefit of E-textiles. Hence, the ideal encapsulation techniques for E-textiles should protect electronic circuitry, while preserve breathability property of textile.

Lastly, the electrical functionalizations by incorporating conductive or semiconductor materials at the fiber level are the promising solutions for E-textile development [66]. Since fiber is the fundamental unit of textile, each fiber can be served as an components for the complex E-textile devices, such as sensors and actuators [66], textile-based displays [25], energy harvesting and energy storage devices [67, 68]. These E-textile devices should provide enough air ventilation without sacrificing their functionality.

In summary, several challenges in the electronic textile development are needed to be addressed for the complete integration of electronic devices and textiles. At present, the embroidered contact between conductive and electronic component is not reliable and inefficient in mass production. These problems could be solved by developing electronic fibers as a building block for textile-based electronic construction. As fiber is a fundamental unit in textile, electronic fibers will create numerous opportunity to functionalize E-textile at any level of integration from fibers to garments. Hence, the studies on the electronic fiber fabrications are the forefront of the advanced E-textile research. The fiber properties and the fiber functionalization technique will be reviewed in the next section.

2.3 Fiber functionalization

Fundamentally, fiber is a material with diameter or thickness smaller than 250 μm and aspect ratio larger than 1000 [69]. The fiber production in textile industry conventionally composes of three main steps: spinning, drawing, and post-treatment process [70]. The spinning is a process, where polymer solution is extruded through a spinneret and solidified into the fiber by either wet spinning, dry spinning, melt spinning, or electrospinning. Then as-spun fibers are drawn to increase crystallinity and fiber strength. Finally, fibers are heat-treated and/or coated to meet the requirements.

These fiber production processes also apply to the electronic fiber production. Instead of natural fibers or polymers, metals, semiconductors, conductive polymers, and carbon derivatives are raw materials for electronic fiber productions. The electronic fibers can be functionalized during either coating process or spinning process, which can be categorized as extrinsic and intrinsic modification respectively [25, 66].

2.3.1 Extrinsic modification

The extrinsic modifications of the fibers are processed after the fiber production. The deposition layer can be either thin film or thick film depending on the deposition method. For thin film deposition, the deposition techniques from microelectronic fabrication such as physical vapor deposition (PVD), chemical vapor deposition (CVD), atomic layer deposition (ALD), electroplating and sputtering can effectively deposit thin film electronic materials on fiber surfaces [18].

As for thick film deposition, dyeing and printing techniques in textile industry are viable techniques for fiber surface modification. Dyeing process is a process where fibers absorb color pigments via intermolecular interactions or chemical bonding with functional groups on fiber surface [70]. Instead of conventional dyes in the textile industry, metal and semiconductor nanoparticles, carbon derivatives and conductive polymers, are used to coat electrical fibers [18]. These electronic dyes are usually mixed with elastomeric polymer such as silicone, epoxy, polyesters, and fluorine rubber to be compatible with screen printing process [71-74], and thick

film coating [75-79].

These extrinsic modifications of the fibers have significant roles in the flexible electronic device fabrications, such as energy harvest and energy storage devices. As these devices require an electron transfers between different materials, the electronic fibers can be fabricated from two main approaches including twisting and multiple layer deposition [25]. The twisted structures utilized the different electrical properties of two or more different coated fibers to construct the electronic devices, for example, the twisted titanium dioxide (TiO₂)-coated stainless steel and platinum wire counter electrode for the dye-sensitized solar cell [80], and the twisted carbon fiber for lithium-ion battery [81]. The second approach was to fabricate the multiple material layer on the fiber surface, for example, the fiber-shaped perovskite solar cell, which composes of stainless-steel fiber, TiO₂ nanoparticles, perovskite material, and carbon nanotube sheet [82]. Figure 3 demonstrates the triboelectric nanogenerator design, which are the twisted zinc oxide nanowire coated fibers [83] and the multiple layer deposition of zinc oxide nanorod and metal electrode on the fiber surface [84].

Although extrinsically modifications are promising techniques, the multilayer structures decrease tensile strength, percent of elongation and flexibility of the fiber [20-22]. In addition, the multiple deposition steps and assembly processes of the electronic fiber fabrications cause the difficulty in the mass production of the microfiber devices. These disadvantages of extrinsic modifications lead to the active research on the intrinsic functionalization of electronic fibers, which potentially serve as the building block for the electronic textile construction.

Figure 3 Designs of electronic fiber devices: 1) Twisted design [83] and 2) Multilayer design [84]

2.3.2 Intrinsic modification

Instead of using surface modified fiber for electronic fiber fabrications, electronic fibers can be directly produced from raw materials using spinning techniques from traditional fiber fabrication process including wet spinning, dry spinning, melt spinning, and electrospinning [27]. Wet spinning is a process that concentrated polymer solution was diluted into the coagulating bath and form fiber shape. On the other hand, dry spinning process apply high pressure to eject polymer solution through a die. Then solvent is evaporated from polymer jet in warm air or inert gas. In the melt spinning, polymers are melted by heat in the absence of solvent and solidified after passing through the spinneret. Last but not least, the electrospinning utilizes the electrical force to eject the polymer solution or molten polymer from the die to the collector with a broad range of fiber diameter from nanoscales to microscale [85].

As these techniques have been developed based on polymer fiber production in textile industry, the intrinsic electronic fiber productions are inevitably involved with the polymerization mechanism of the polymers. Metal and semiconductor nanoparticles and carbon derivatives are possible to be produced in fiber-shaped by incorporating these materials into the polymer matrix. For example, silver nanowires and silver nanoparticles were incorporated in elastomeric polymers through the ejection of the composite fiber in coagulating bath [23]; the coaxial fibers for multicolor display were fabricated from the composite of polypropylene, carbon nanotube, TiO_2 and thermochromic materials through melt spinning methods [26].

Among these spinning techniques, electrospinning technique is the most efficient technique for microfiber production at laboratory scale due to their simplicity, versatility and low-cost as compared in Table 1[27]. Therefore, the electrospinning setup is selected for the high-performance gas sensing microfiber fabrication in this project. The fundamental theory on the fiber formation of the electrospinning, the important fabrication parameters and the applications of electrospinning in the electronic textile will be discussed in the next section.

Table 1 The comparison of fiber production parameters [27]

Consideration factors	Wet spinning	Dry spinning	Melt spinning	Electrospinning
Solvent requirement	Yes	Yes	No	Yes
Temperature	Low	Low	High	Low
Ejection forces	High Pressure	High Pressure	High Pressure	Electrical force
Fiber size	Nanoscales to Microscales	Microscales to Microscales	Microscales	Nanoscales to Microscales
Quantity of fibers	Large	Large	Large	Small
Fiber Morphology	Single fibers Coaxial fibers	Single fiber	Single fibers, Coaxial fibers,	Single fibers, Coaxial fibers, Porous fibers, Hollow fibers, etc.
Production cost at Laboratory-scale	High	High	High	Low

2.4 Electrospinning

Electrospinning is a process, where polymer solution or molten polymer is ejected from a syringe to a collector under high electric field between syringe tip and conductive collector as shown in Figure 4. The first component of the electrospinning system is the syringe, which is installed on the syringe pump for controlling flow rate. The conductive syringe tip and collector are connected to high electrical potential supply in the range of 10 – 50 kV. After applying an electrical potential to the system, liquid polymer is ejected from syringe to collector under electrical force. During the ejection, solvent in polymer jets evaporate, and subsequently polymer fibers are solidified. The fibers with diameters in the range of nanoscale to microscale are deposited as a nonwoven membrane on the collector.

Figure 4 Electrospinning schematic and ejected polymer solution from syringe tip

2.4.1 Fiber formation of electrospinning

Although electrospinning process seem to be straightforward, the fiber formation involve complex interaction between electrical force on electrically charged molecules and surface tension of polymer solution. In theory, electrospinning or electrohydrodynamical phenomena compose of four steps: droplet formations, development of linear jet, bending deformation and instabilities and fiber deposition as illustrated in Figure 5 [86-92].

Droplet formation

Droplet formation is the first step of electrospinning. Normally, polymer stream from syringe tips formed droplet because of the surface tension of the polymer solution and the statistical perturbation of the liquid flow [85]. However, upon applying the electrical potential between syringe tip and conductive collector, the electrical force on the charged molecule on polymer solution surface balance the surface tension of the polymer stream thereby stabilizing the droplet, so-called “Taylor cone” [86, 93]. This conical droplet formation on orifice is governed by the dielectric permeability, the surface tension and the charge density of the polymer solution. When the applied electric field overcome the surface tension of the liquid droplet, the straight liquid jet start ejecting from tip of droplet as shown in Figure 5.

Figure 5 Fiber formation of electrospinning (modified from Wendorff, et al. [85] and Reneker and Yarin [92])

Development of linear jet

After polymer solution is ejected from the droplet, the ejected polymer stream elongates and thins toward the collector under the effect of Coulomb force, which is a pulling force from the electric field on the charged molecules inside polymer jet. At this moment, surface tension and Coulomb force are two counterpart forces on the surface of polymer jet, maintaining the fiber formation [92]. As the Coulomb force requires the charged particle in polymer jet to draw the polymer fiber to the collector, nonpolar polymers or insulator materials, therefore, are not suitable for electrospinning. To spin such materials, the additional charged molecules, such as polar solvent, metal ion, metal nanoparticles, are necessary in the polymer system. On the other hand, if the liquid polymer does not have enough surface tension to maintain the fiber shape, the instabilities will occur inside the polymer jet and then cause either bead formation in fiber or droplet formation, which results in an electrospraying instead [89]. Therefore, charge density inside polymer must be balanced with their viscosity to maintain fiber formation during the electrospinning process.

Bending deformation and instabilities

After the straight polymer jet is formed in the second stage, the electrified polymer jet starts

developing the whipping loop instead of depositing on the collector as a straight line. This behavior of the polymer jet is driven by two major instabilities inside polymer jet including bending instability (whipping instability) and charge-driven axisymmetric instability [88-90]. The dominant instability in the polymer stream depends on the local electric field near the polymer jet, which is determined by the surface charge distribution, viscosity, and surface tension of the polymer jet [89]. If the local electric field is dominated by static charge density, the long-wave perturbation and lateral velocity of the polymer jet will cause fiber to bend and form the spiral trajectory [88]. The bending instability polymer jet will repeat itself until the polymer fiber solidifies. On the other hand, if the external tangential force is dominated in the local electric field on fiber surface, the axisymmetric instability will create beads along fibers due to the random perturbation in diameter along the fiber strand [89].

These understanding of the instability of the fiber formation is crucial for tailoring microfiber morphology. The customized electrospun microfiber membrane can be fabricated by controlling polymer composition and configuration of electrospinning setup. For example, the bead formation of the electrospun fiber was controllable by selecting the appropriate applied electric field and corresponding polymer flow rate as shown in Figure 6.

Figure 6 Effect of feed rate and applied an electric field on fiber formations (modified from Wendorff, et al. [85], Reneker and Yarin [92], and Hohman, et al. [87])

Fiber deposition

Finally, the solidified fibers deposit on the counter collector electrode. The deposition pattern of the polymer fiber is strongly dependent on the structure of the collector, which determines the electrical field on the polymer fiber. The electrospun fibers are typically deposited as nonwoven membrane on planar electrode [85], while the patterned membrane require special electrode designs such as patterned conductive collectors [94, 95] and direct write electrospinning [96].

2.4.2 Electrospinning configuration parameters

As discussed in the previous section, the fiber formation in the electrospinning process is closely related to the properties of polymer solution and the electric field in the electrospinning system. The parameter in electrospinning systems can be categorized into three groups including polymer solution, machine configuration, and ambient environment as summarized in Table 2 [97, 98].

Table 2 Electrospinning parameters [98]

Solution properties	Machine configuration	Environment
Material selection	Applied potential	Temperature
Solvent selection	Tip-to-collector distance	Humidity
Concentration	Flow rate	Pressure
Viscosity	Transverse movement	
Surface tension	Side-wall electrode	
Permittivity	Syringe design	
Conductivity	Counter electrode design	

The property of material solution is the first consideration for electrospinning process. Most of the electrospinning use polymer solutions for microfiber production due to their suitable viscoelasticity, long molecular chain and preferably intermolecular interaction [99]. Polymer solutions are also used as carrier matrix for the electrospinning of metal and semiconductor nanoparticles. The viscosity, the surface tension, and the charge density of the mixture solution

must be optimized during the solution preparation to fit the specific polymers, solvents and particles.

For electrospinning machine configuration, tip-to-collector distance, applied potential, solution flow rate, collector rotation speed, transverse movement, height of collector and syringe size are considerable parameters. These parameters mainly affect the electric field on solution surface as discussed in the fiber formation section 2.4.1. With the progression in the electrospinning research, several electrospinning setups have been proposed to control the morphology, the alignment and the deposition pattern of microfibers on substrate [100, 101]. Some unique syringe design can even mass produce coaxial microfibers by ejection of multiple fiber simultaneously [102].

Finally, environmental conditions, especially temperature and humidity, affect the electrospinning parameters. For example, higher electrical potential is required in high humidity electrospinning chamber due to high permittivity of water vapor; or high humidity and low temperature decrease evaporation rate of the solvent resulted in larger fiber diameters. Therefore, these parameters must be carefully controlled for the repeatability of the microfiber production.

2.4.3 Electrospinning in E-textiles

The nonwoven electrospun microfiber membrane are traditionally used as windproof, waterproof, thermal insulation, antibacterial, self-cleaning and filtering fabrics owing to the great variety of raw materials and large surface to volume ratio of microfiber membrane [85]. These properties of nonwoven electrospun microfiber are also beneficial to electronic textile fabrications. The conductive nano/microfiber membrane for high performance electrodes can be electrospun from conductive polymers [103], metals [104, 105], and carbon derivatives [106]. In addition, the microporous structure of electrospun microfiber membrane provide large deposition volume for nanomaterials in the energy harvesting and storage devices [107, 108] and ultrasensitive sensors [28, 29].

2.5 Electrospun chemical gas sensor

Among several interesting applications of electrospun electronic fibers, the electrospun nano/microfiber membrane for wearable gas sensors in personal protective equipment (PPE) is challenging. Lightweight and ultrasensitive gas sensors are appealing to soldier, firefighter and other extreme occupations in dangerous environments [30, 32, 109] as well as people in urban areas where air pollutions are severe worldwide [110].

Gas sensors compose of two crucial components: gas recognition materials and signal transduction devices. The interaction between recognition materials and targeted gas through physical adsorptions or chemical reactions cause the change in mass, temperature, or electrical properties of the recognition layers. Then these changes from gas recognition layer can be converted into detectable signals either optically or electrically by transducers such as electrodes and optical fibers respectively. Therefore, gas sensors are categorized into two categories based on transduction signals: optical gas sensors and electrical gas sensors.

In literature [111], optical gas sensors utilize the spectroscopy to determine several gas species simultaneously based on their characteristic wavelength absorption. The absorption intensity of the corresponding wavelength is then converted to the gas concentration in the range of part per million (ppm) to part per trillion (ppt). Since these systems required high-power laser at a specific wavelength and precise wavelength absorption system for high sensitivity and excellent selectivity, high-performance optical gas sensors are more suitable as the analytical instrument in the laboratory or for the safety control in the building rather than wearable devices.

For the electrical gas sensors, the alteration in electrical properties of gas recognition materials such as electrical current, electrical potential, work functions, and resistance are the principle of electrical gas sensors [112, 113]. The ultrasensitivity, light weight, and small footprint electrical gas sensors have been successfully developed for wearable devices recently [5]. Some researchers embroidered miniaturized gas sensors on the fabric circuitry to create smart protective garment [25, 66], while others coated gas sensitive materials such as metal oxides (e.g. SnO_2 , TiO_2 , and ZnO) [114], conductive polymers (e.g. polypyrrole (PPy) or polyaniline (PANI)) [33-35], and carbon nanostructures (e.g. carbon nanotube and graphene)

[36-38] on the fabric surface. However, these modification methods commonly suffer from the deterioration of the sensing elements and the poor interconnection between sensors and fabric circuits as discussed in extrinsic modification in section 2.2. Hence, gas sensing fiber fabrication are the promising approach to intrinsically improve the stability of gas sensing fabric devices.

Several gas sensing microfiber membranes have been produced by electrospinning. The as-spun microfiber membranes have large specific surface area and tunable pore size giving rise to ultrasensitive gas sensing responses [115]. Unfortunately, the fiber-shaped gas sensors are not yet successfully developed because of limitations in material properties including the brittleness of metal oxides, the poor long-term stability of conductive polymers and the high production costs of carbon nanostructures [25]. Hence, the current trend of gas sensor fabrications is moving toward composite fibers to integrate flexibility of organic conductive fiber with high sensing performance of metal oxide materials [39, 40].

2.6 Electrospinning of titanium dioxide gas sensing fiber

One of the well-known materials for electrospun gas sensors is titanium dioxide (TiO_2) due to their chemiresistor property, which is the change in resistance of TiO_2 upon the presence of gas. The interaction between the target gas and the recognition molecule occurred at three hierarchical levels of the sensing layer: the grain surface, the grain boundaries, and the gas sensing body as illustrated in [113].

Figure 7 Gas sensing mechanism of semiconductor gas sensors [113]

At the grain surfaces, oxides on crystallite surface interacts with target gas. For oxidizing gases, oxygen (O_2) molecules from the environments are absorbed by metal oxide grain. Then the absorbed oxygen molecules induce the surface charge depletion and increase the work function of metal oxide, thereby increasing resistance of the material. On the other hand, if the metal oxide exposes to the reducing gases, such as hydrogen (H_2) gas as illustrated in Figure 7(a), the reduction will happen on the surface and decrease the resistance of the material. The changing of work function from redox reaction on the surface of TiO_2 grain surface alter electrons transport through the grain boundaries in Figure 7(b), which is modeled by double Schottky barriers. At this level, the grain size, carrier mobility, and the doping of the semiconductor play important roles in the sensitivity of the gas sensors. If diameter of TiO_2 grain was larger than the critical value, the resistivity will decrease and vice versa [113]. Finally, the structure of the gas sensing layers, and the temperature affect the diffusion rate of the target gas to the sensing elements as demonstrated in Figure 7(c). If the reaction rate on TiO_2 surface is fast and the diffusion rate of target gas is slow, the gas cannot be detected reliably. Therefore, porosity and diffusion rate of the gas to TiO_2 microfiber should be optimized to achieve high performance gas sensors.

The electrospinning of TiO_2 microfiber was first introduced by Li Dan and Xia Younan in 2003 [116]. They electrospun the mixture of TiO_2 precursor in poly (vinyl pyrrolidone) (PVP) to produce microfiber membrane. Then PVP was burnout and TiO_2 microfiber was crystallized during the calcination process. The large surface area of TiO_2 microfibers and the controllable pore size of the electrospun membranes were appealing properties for the high performance electronic devices such as photocatalytic [117-125], photovoltaic [126-129], and sensing applications [130-146].

There are two main approaches on the electrospinning of the TiO_2 nanofibers based on the solution preparation: electrospinning-assisted sol-gel synthesis and the particle dispersion technique [147, 148]. For the electrospinning-assisted sol-gel synthesis, TiO_2 precursors, i.e. Titanium (IV) alkoxide derivatives, are dissolved in the carrier polymer solution [116]. These precursors are polymerized and oxidize to TiO_2 nanofibers during the calcination process. On the other hand, in the particle dispersion technique, metal oxide nanoparticles are

homogeneously dispersed in the carrier polymers and merge into microfiber after calcination process [149, 150].

Both electrospinning-assisted sol-gel synthesis and nanoparticle dispersion techniques require the carrier polymer as a medium during electrospinning process. Since this carrier polymer are decomposed during the calcination process at high temperature, polymers, solvents and precursors should be non-toxic substances. For the particle dispersion technique, the mean diameter of electrospun polymer fiber should be larger than the size of TiO₂ nanoparticles to incorporate nanoparticles inside the microfibers. The example applications of each fabrication technique are summarized in Table 3.

One of the potential polymers, which meet both criteria, is poly (vinyl pyrrolidone) (PVP). PVP is a water-soluble polymer used in the regenerative medicine, pharmaceutical, and textiles [151]. It also has been used as a sacrificial matrix for the electrospinning of metal oxide nanofibers [116]. According to preliminary study, we have successfully fabricated the electrospun microfibers with the mean diameter of diameter 1 – 2 μm as shown in

Figure 8 [152]. Therefore, PVP was selected as a carrier polymer for TiO₂ nanofiber fabrication in this project.

Figure 8 FE-SEM images of PVP microfibers at magnification of a) 1k, b) 10k [152]

Table 3 Electrospinning methods for titanium dioxide microfiber fabrication

Techniques	Polymers	Solvents	Applications	Ref.
In situ sol-gel synthesis	PVP	Acetic acid	Photocatalytic	[116-119, 124]
		Ethanol	Humidity sensor	[130-134]
			CO sensor	[136, 137]
			NO ₂ sensor	[141, 142]
			NH ₃ sensor	[143]
			Acetone sensor	[144]
			Ethanol sensor	[145, 146]
	PVAc	Acetic acid	Photocatalytic	[24, 122, 126]
		Dimethyl formamide (DMF)	CO sensor	[135]
			NO ₂ sensor	[140]
Nanoparticle dispersion techniques	Copolymer	Ethanol	Photocatalytic	[125]
	PAN	DMF	Photocatalytic	[123, 127, 128]
			NO sensor	[139]
	PVC or PS	DMF	Photocatalytic	[129]
	Nylon-6	Dimethylacetamide		
		Acetic acid	UV blocking,	[153, 154]
		Formic acid	Antibacterial	
	PU	DMF	Photocatalytic	[155]
			Antibacterial	[156]
	PVA	DMF	CO ₂ sensor	[138]
Other methods	Nylon-6	ethanol/water	Photocatalytic	[120]
	PMMA	Acetic acid/ethanol	Photocatalytic	[121]
	PVA	Anhydrous	-	[157]
		ethanol/water		

Chapter 3

Methodology

The electrospinning for gas sensing microfiber fabrication composed of three main studies. First, the dispersion of titanium nitride nanoparticles (TiN-NPs) in water and ethanol was studied to select the proper solvent for particle dispersion preparation. The second study was to fabricate and characterize electrospun TiO₂ microfiber membranes. The effects of electrospinning parameters and the effects of thermal oxidation temperature on the morphology of TiN-NPs in PVP (TiN-NPs/PVP) microfiber membrane and crystallite structure of TiO₂ microfibers were studied respectively. Lastly, the gas sensing properties of TiO₂ nanofibers was examined on carbon monoxide (CO) gas. The design of interdigitated electrode (IDE), the fabrication of gas sensors, and the setup of gas sensor characterization system (GSCS) were explained.

3.1 The study on TiN dispersion in water and ethanol

The nano-sized TiN powders (97%, Oxygen<1.0%, Hefei Kaier) with an average particle size of 20 nm was dispersed in deionized water (DI water) and ethanol with the concentration of 0.01 %_{wt/v}. Then 1%_{v/v} Tween 80 was added into the suspension to study the effect of surfactant on TiN-NPs dispersion. All suspension was vigorously stirred with magnetic bar and sonicated consecutively. The duration of each mixing step was 30 minutes as suggested in literature [158, 159]. Finally, Zeta potentials and particle size distributions were analyzed by zeta potential analyzer (Zetasizer Nano ZSP, Malvern Panalytical).

3.2 The fabrication of TiO₂ microfiber membrane

The fabrication of TiO₂ microfiber membrane was divided into three steps including solution preparation, electrospinning, and thermal oxidation as shown in Figure 9.

Figure 9 the overview of TiO_2 microfiber membrane fabrication

First, TiN-NPs dispersion and PVP solution were prepared in ethanol separately. TiN-NPs concentration of 2%_{w/v}, 4%_{w/v}, 6%_{w/v}, 8%_{w/v}, and 10%_{w/v} were dispersed in ethanol by vigorous stirring at room temperature for 30 minutes. The mixtures were subsequently sonicated for 30 minutes. Meanwhile, 20%_{w/v} PVP solution was dissolved in ethanol by vigorous stirring at 50°C for 1 hour. Then the same volume of TiN-NP dispersion and PVP solution were mixed together at room temperature using magnetic stirrer and sonication bath for 30 minutes in each process. The final concentrations of TiN-NPs/PVP dispersion were 1%_{w/v}, 2%_{w/v}, 3%_{w/v}, 4%_{w/v}, and 5 %_{w/v} TiN-NPs in 10 %_{w/v} PVP solution.

After TiN-NPs/PVP dispersions were prepared, 5 ml of the dispersion was loaded into syringe for electrospinning. As illustrated in Figure 10, the syringe tip size 19G was used for spinneret. The distance between syringe tip and rotational collector was 15 cm. The aluminum foil, glass slide, and interdigitated electrode were attached on collector surface depending on requirements of each characterization method. The flow rate of TiN-NPs/PVP dispersion was set at 1 ml/hour and the rotational speed of collector was 140 rpm. The electrical potential of 20 kV (-4 – 16 kV) was applied between syringe tip and collector for 1 hour. As-spun TiN-NPs/PVP microfibers were annealed at 50°C for 1 hour to remove residual solvent and solidify microfiber.

Figure 10 Electrospinning setup for TiN-NPs/PVP microfiber membrane fabrication

Finally, TiN-NPs/PVP microfibers were annealed in air at 500°C, 600°C, and 700°C for 2 hours using furnace (Laboratory chamber furnace BRF14/5, Elite thermal systems Ltd.) to study the effect of temperature on the thermal oxidation of TiN-NPs to TiO₂. TiO₂ microfiber samples were cooled down for 2 hours before removing from the furnace chamber to avoid thermal stress in the samples. TiO₂ microfiber samples were kept in the desiccator at room temperature and controlled relative humidity of 40-50%.

3.3 Fabrication of TiO₂ microfiber for CO gas sensing

TiO₂ microfiber membrane was fabricated on interdigitated electrode (IDE) to examine gas sensing properties of the microfiber membrane. The electrodes used in this study were 9 pairs of gold IDE on aluminum oxide (Al₂O₃) substrate. The dimension of the substrate was 18 mm x 18 mm and the electrode dimensions was 300 μm in width with 300 μm spacing between electrode as illustrated in Figure 11.

Figure 11 The schematic of gold interdigitated electrode

For the deposition of TiO₂ microfiber membrane, 6%_{wt/v} TiN-NPs in ethanol and 20%_{wt/v} PVP solution were mixed with the same volume by vigorous stirring at room temperature for 30 minutes. The final concentration of TiN-NPs/PVP dispersion was 3%_{wt/v} TiN in 10 %_{wt/v} PVP solution. The same electrospinning process was repeated as described in Section 3.2. In addition to the previous setup, gold IDEs were attached on top of aluminum foil on the collector using double side adhesive tape. The syringe pump also moved repeatedly in transverse direction with

the moving distance of 200 mm and movement speed of 100 mm/min to ensure a uniform coating on the substrate. Electrical potential of 20 kV (-4 – 16 kV) between syringe tip and collector was applied for 4 hours. The deposited IDEs were annealed at 50°C for 1 hour to remove residual solvent and solidify the membrane. Finally, the samples were annealed in the furnace at 700°C for 2 hours and cooled down for 2 hours to transform TiN-NPs/PVP microfiber to TiO₂ microfiber.

3.4 Material characterization

Surface morphology, material composition, crystalline structure, phase composition and thermal oxidation behaviour of both TiN-NPs/PVP microfiber and TiO₂ microfibers were studied using several characterization methods. A description of each characterization method is given in the following section.

3.4.1 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX)

Surface morphology of the samples was investigated using field emission scanning electron microscope (FESEM, JEOL7600). In addition, material composition under the area of interest was examined using Energy Dispersive Spectroscopy (EDS/EDX, Oxford instruments). Finally, fiber diameter and porosity of the microfiber membrane were analyzed from the obtained SEM images using ImageJ program with DiameterJ plug-in [160, 161].

3.4.2 X-ray Diffraction (XRD)

The crystallite structure of TiO₂ microfibers at room temperature were examined using X-ray diffractometer (PANalytical Empyrean) with Cu K-alpha radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. The 2-theta detector scanned from 10 to 90° with step size of 0.02° and time step of 300 milliseconds. The crystallite size of anatase and rutile in TiO₂ microfiber membrane was estimated from XRD patterns using Scherrer's equation [162]

$$D = \frac{K\lambda}{\beta \cos \theta} ,$$

where K is Scherer constant (K usually taken as 0.9 for particle), λ is the wavelength of the radiation, β is full width half maximum (FWHM) of the diffraction peak, and θ is the diffraction angle.

The anatase ratio in TiO₂ microfiber membrane was calculated using Spurr's equation[163]

$$f_a = \frac{1}{1 + 1.26 \frac{I_R}{I_A}} ,$$

where f_a is the fraction content of anatase, I_A and I_R are intensity of anatase (101) and rutile (110) respectively.

3.4.3 Differential thermal analysis (DTA) and thermogravimetric analysis (TGA)

The material transitions of TiN-NPs/PVP microfibers to TiO₂ microfibers were observed using the simultaneous DTA-TGA thermal analyzer (DTG-60H, Shimadzu). The temperature range of 30 to 1000°C with increasing temperature of 10 °C/minute in air atmosphere was set for DTA-TGA thermal analyzer. The endothermic and exothermic reaction in the sample were analyzed by differential thermal analysis (DTA) and the changing in weight of the sample was compared with the weight of standard alumina powder reference in thermogravimetric analysis (TGA). Therefore, combining DTA-TGA plots together as a function of temperature provided more insight to material transitions of the sample including decomposition of PVP, thermal oxidation and crystallization of TiO₂.

3.4.4 Gas sensing characterization of TiO₂ microfiber membrane on interdigitated electrode

Gas sensor characterization system (GSCS) was setup in Nanomaterials Laboratory at the School of Electronic and Electrical Engineering (EEE). In this system, the sample was placed under the test gas flow and on the heating stage in the testing chamber as illustrated in Figure

12. The custom-built bronze probes directly contacted sample electrodes and connected to the Keithley 236 source measurement unit (SMU). The concentration of CO in test chamber was controlled by MKS1179A mass flow controller (MFC) and MKS247C 4-Channel-readout. The heating and cooling rate of the sample was controlled by Linkam TMS93 temperature controller. These measuring and control instruments interfaced with computer using National instruments Labview 7.1 program. The resistance response of the sample was stimulated by applying constant voltage of 5 Volts to sample. Finally, time, gas concentration, temperature and resistance response were recorded with sampling rate of 2 seconds.

Figure 12 The schematic of gas sensing characterization system (GSCS)

For background scan, the temperature response of TiO_2 microfiber membrane on interdigitated electrode was first obtained under the constant flow of dry air at 200 sccm. The temperature was increased at a ramping up rate of 3°C per minute from room temperature to 350°C and held for 10 minutes before decreasing to room temperature at a ramping down rate of 3°C per minute. Finally, the temperature was held at 30°C for 30 minutes. This process was repeated for 2 cycles.

The change in resistance of the sample in the presence of CO gas were collected in the second study. The sample was heated up from room temperature to 350°C under the constant flow of dry air at 200 sccm with the ramping up rate of 2°C per minute. After the temperature was stabilized at 350°C for 1 hour, 200 ppm CO balanced with air was purged on the sample for 1 hour, followed by dry air purging for 2 hours. Finally, samples were cooled down to room temperature at a cooling rate of 5°C per minute.

The performance of the TiO₂ microfiber membrane were evaluated from the resistance responses as performed in literatures [135, 140, 142, 164]. The response time was defined as the time required for sensor to reach to 90% of the minimum resistance upon exposure to CO gas, while the recovery time was defined as the time required for sensor to return to 90% of the baseline resistance after removal of the gas.

The sensitivity and noise level of the base line resistance were calculated from these following equations

$$Sensitivity = \frac{R_{air}}{R_{CO}} ,$$

$$noise\ level\ of\ baseline\ resistance = \frac{3 \times \sigma_{air}}{R_{air}} ,$$

where R_{air} and σ_{air} are the average resistance and the standard deviation of the sensor before exposure to CO gas respectively, and R_{CO} is the average resistance of the sensor after exposure to CO gas.

Chapter 4

Result and Discussion

4.1 The study on TiN dispersion in water and ethanol

TiN-NPs dispersions in deionized water (DI water) and ethanol with and without Tween80 are shown in the Figure 13. Only TiN-NPs in the mixture of Tween80 and ethanol precipitate at bottom of the test tube, while they are successfully dispersed in the other solutions.

Figure 13 TiN-NPs dispersions in different solvent: a) TiN-NPs in DI water, b) TiN-NPs in Tween80/DI water, c) TiN-NPs in ethanol, and d) TiN-NPs in Tween80/ethanol

This phenomenon can be explained using nanoparticle dispersion theory [165]. In the colloidal solution system, the stability of particle dispersion depends on the summation of the force acting on the surface of particles. The Van der Waals force from molecular weight creates the attraction force between molecules in solution. Simultaneously, ion molecules in aqueous solution accumulate on the surface of TiN-NPs create the electrostatic repulsion force between particles preventing the agglomeration of nanoparticles. Therefore, the stability of the colloidal system is typically indicated by surface potential of the particle, called “Zeta potential”. The minimum zeta potentials for the stable colloidal system are suggested at ± 30 mV [165].

Table 4 Zeta potentials and Particle size distribution of TiN in DI water and Ethanol

TiN dispersion methods	Deionized water (DI)		Ethanol	
	without Tween80	Tween80	without Tween80	Tween80
Zeta potential (mV)	-0.0623	-33.9	-35.4	-0.186
Average size distribution (nm)	2878	828	1172	sedimentation

As shown in Table 4, zeta potential of TiN-NPs in pure DI water is -0.06 mV and significantly increases to -33.9 mV after adding Tween 80 to the system. High zeta potential of TiN-NPs in the presence of organic surfactant prevents the agglomeration of TiN-NPs in DI water. As a result, the particle size distribution of TiN-NPs in the mixture of DI water and tween 80 is significantly smaller than the particle size in DI water.

This result agrees with the previous study on the TiN-NP dispersion [158]. In the aqueous solution, the organic surfactant i.e. Tween 80 attaches on the nanoparticle surface and increases the hydrophilic property on the particle surface [158, 159]. The adsorbed water molecules on the surface of nanoparticles result in the increase of the zeta potential of particles. In addition, the extension of the surfactant molecule on the nanoparticle surface acts as the barrier, called “steric hindrance”, which further stabilize the particle dispersion. Therefore, the aqueous system requires the organic surfactants to facilitate and stabilize nanoparticle dispersion.

In contrast to the results from the aqueous solution, TiN-NP dispersion is stable in pure ethanol with zeta potential of -35.4 mV, which is sufficient to prevent the agglomeration of the nanoparticles [165]. However, the addition of Tween80 also leads to the particle sedimentation as shown in Figure 13(d). This phenomenon is related to the orientation of Tween80 on the particles surface. Non-polar tails of Tween80 typically interact with nanoparticle surface and hydrophilic heads expose to the environment [158, 159]. Although this orientation is beneficial to the dispersion in aqueous solution, the exposure of the polar head of Tween80 in the organic system potentially lead to the insolubility of nanoparticle in the organic solvent system as found in this experiment.

To avoid the complication of electrical double layer in the aqueous system, ethanol is selected to be the dispersion medium for TiN nanoparticles in the subsequent experiment.

4.2 Fabrication of TiN/PVP composite microfibers

Uniform dispersion of TiN-NPs in ethanol is crucial for the colloidal electrospinning [150]. Preliminary study found that 8%_{wt/v} of TiN-NPs in ethanol is the maximum concentration for TiN-NPs dispersion in ethanol. At 10%_{wt/v} of TiN-NPs in ethanol, TiN-NPs cannot disperse in ethanol because the volume of TiN-NPs exceed the volume of ethanol. Therefore, results from the concentration of 5%_{wt/v} TiN-NPs in PVP solution, which was prepared from the mixture of 10%_{wt/v} of TiN-NPs and PVP solution, are excluded.

TiN-NPs/PVP microfibers are successfully synthesized from TiN-NPs/PVP dispersions with concentration of 1%_{wt/v}, 2%_{wt/v}, 3%_{wt/v} and 4%_{wt/v}. The colors of the deposited membrane are darkened with increasing TiN-NPs contents in microfiber membrane. Although 1%_{wt/v} and 2%_{wt/v} TiN-NPs in PVP solution can produce microfibers, TiN-NPs are not distributed uniformly throughout the collector surface. As TiN content increases to 3-4%_{wt/v}, the distribution of TiN-NPs in the fiber improves significantly.

SEM images of the composite microfibers are demonstrated in Figure 14(a)-(d). TiN-NPs are successfully incorporated into PVP microfibers. The fiber diameters are found in the range of 200 nm to 700 nm. As shown in Figure 14(e), the average fiber diameters tend to decrease with the increasing of TiN-NPs content in PVP polymer solutions. The decreasing of average fiber diameters should be resulted from the increasing of surface conductivity of TiN-NPs/PVP suspension. As a result, high electrical force acting on the polymer jet during electrospinning reduces diameter of electrospun TiN-NPs/PVP microfiber [147, 153].

Figure 14 FESEM image of TiN-NPs/PVP microfiber from different TiN-NPs/PVP concentration: a) 1%_{wt/v}, b) 2%_{wt/v}, c) 3%_{wt/v}, d) 4%_{wt/v}; and e) the comparison of the average fiber diameter from each concentration.

4.3 Thermal oxidation of TiN/PVP microfiber

After heating TiN-NPs/PVP microfibers in the air at 500 – 700°C, TiN-NPs/PVP microfibers change color from black to white as shown in Figure 15, suggesting the successful oxidation of TiN-NPs to TiO₂ nanostructures.

Figure 15 Thermal oxidation of TiN-NPs/PVP microfibers to TiO₂ microfibers

The effects of temperature on the transformation of TiN/PVP microfibers are studied from the DTA-TGA analysis. The decomposition of electrospun PVP microfibers composes of two steps as shown in Figure 16(a). The first step is the evaporation of the absorbed moisture on PVP microfibers at 50°C to 100°C. Beyond 200°C, decomposition of PVP microfiber begins with a sharp exothermic peak from DTA curve at 330 °C. The decomposition of PVP microfibers continues until 700°C. There are no significant weight changes afterward. This result agrees with the previous study on the thermal decomposition of PVP microfibers [166-168].

Figure 16 Thermal analysis of (a) PVP microfibers and (b) TiN/PVP composite microfibers

Different from DTA-TGA diagram for pure PVP microfiber, TGA diagram of TiN-NPs/PVP microfibers consist of three steps as shown in Figure 16(b). The first approximate weight loss of 15% is found at the temperature between 50°C to 100°C because of the desorption of moisture inside TiN-NPs/PVP microfibers. Then PVP microfibers start decomposing at temperature of 300°C. At this temperature, the exothermic peak from PVP decomposition is less than the peak from pure PVP microfibers. This alteration of DTA curve could be resulted from the initiation of thermal oxidation of TiN-NPs as reported by Saha and Tompkins [169]. They found that in the initiation period of thermal oxidation of TiN at temperature 350°C, thin layer of TiO₂ was gradually formed on the surface of TiN and change the crystallite structure from amorphous to crystalline. As the crystallite formation is an endothermic reaction, it could absorb the released energy from PVP decomposition thereby decreasing exothermic peak in DTA curve.

Finally, the third shoulder of TGA curve occurs at the temperature range of 450 °C to 550 °C. High exothermic reaction at 540 °C in DTA curve indicates the oxidation of TiN to TiO₂ as reported by several studies [127, 170-172]. PVP matrix is completely decomposed after 600 °C and solid TiO₂ remains in the sample holder with the weight of 20% of initial weight.

Figure 17 FESEM image of TiO₂ microfibers from TiN-NPs/PVP microfibers with different TiN contents: a) 1%_{wt/v}, b) 2%_{wt/v}, c) 3%_{wt/v} and d) 4%_{wt/v}

FESEM images reveals mesoporous nanofiber of TiO₂ nanostructures on aluminum foil as shown in Figure 17. In Figure 17(a), 1%_{wt/v} TiN-NPs/PVP microfiber cannot sustain the fiber-shaped TiO₂ after thermal oxidation, and TiO₂ nanoparticles are found on the surface of aluminum foil instead. TiN-NPs/PVP microfibers with the minimum content of 2%_{wt/v} TiN/PVP can form TiO₂ microfiber after thermal oxidation as shown in Figure 17(b)-(d). The higher content of TiN-NPs in PVP microfibers, the more stable mesoporous TiO₂ microfibers form on the substrate. These results agree with the previous studies on the colloidal electrospinning of TiO₂ nanofibers, where the concentrations of TiO₂ nanoparticles in polymer matrix in the range of 1 – 8 %_{wt/v} was suggested for synthesizing TiO₂ microfibers [138, 154, 155].

The material compositions of TiO₂ microfibers with different calcination temperature are analyzed using EDX analysis. In Figure 18(a)-(b), aluminum peaks are found in the samples prepared at 500 °C and 600 °C because TiN-NPs/PVP microfibers are deposited on aluminum foil. However, since aluminum foil has melting point at 660 °C, the 700 °C-treated sample is

deposited on gold IDE instead thereby presenting gold peaks in EDX result as shown in Figure 18(c). The small carbon peaks in all samples arise from adhesive carbon tape on the SEM sample holder.

The peaks of titanium and oxygen present in all EDX results in Figure 18 confirm the thermal oxidation of TiN-NPs/PVP microfiber to TiO₂ nanofibers. Besides titanium and oxygen, the nitrogen peaks are found in all EDX results. This nitrogen composition in TiO₂ nanofibers could be either the remaining TiN nanoparticles or N-doped TiO₂ since the similar EDX pattern was reported in the previous study on the N-doped TiO₂ nanorods [173]. Although the thermal oxidation at 700 °C is expected to decrease the nitrogen content in TiO₂ microfiber, nitrogen molecules remain in TiO₂ microfiber as shown in Figure 18(c). The N-doped TiO₂ microfibers could theoretically improve the gas sensing performance of TiO₂ as report in literature [174, 175]. Therefore, the thermal oxidation of TiN-NPs/PVP microfiber is the promising method to produce high performance gas sensing TiO₂ microfiber membrane.

Figure 18 EDX results of TiO₂ nanofiber from TiN-NPs/PVP microfibers at different temperatures: (a) 500°C, (b) 600°C, and (c) 700°C. Insets are the selected location of the analysis

4.4 Crystallization of TiO₂ microfiber

The absence of XRD peaks (200), (111), and (220) of TiN crystallite after oxidized at 500 °C and 700 °C confirms the transformation of TiN crystallite to TiO₂ crystallite as shown in Figure 19. At 500 °C, anatase TiO₂ is the dominant phase in TiO₂ microfiber with the anatase ratio of 0.74±0.03. On the other hand, when the temperature increases to 700 °C, the characteristic XRD peaks of rutile phase increase significantly. Rutile TiO₂ becomes the dominant phase with the calculated anatase ratio of 0.32±0.05.

Besides phase transformations, the increasing temperature also increases the size of both crystallite phases as XRD peaks from the sample with oxidizing temperature at 700 °C become narrower. The estimated sizes of anatase crystallite and rutile crystallite increase from 16 nm to 20 nm as summarized in Table 5. The growths of crystallite phase inside TiO₂ nanoparticles lead to the coarsening of TiO₂ nanoparticle in the microfiber as shown in Figure 20.

Figure 19 XRD patterns of TiN-NPs/PVP microfiber membrane and TiO₂ microfiber after oxidizing at 500°C and 700°C

The phase transformation of TiO₂ from anatase to rutile when increasing the temperature agrees with the previous studies on TiO₂ microstructure fabrication [125, 176-181]. Zhang, H. and J. F. Banfield called this phenomenon as “the size-dependent stability of polymorphic TiO₂ crystalline” [182]. They explained that anatase phase is the most stable phase when the particle

size is less than 11 nm, while rutile phase is the most stable phase when the particle size larger than 35 nm. In our study, as TiO₂ crystallite size is in the range of 16 – 20 nm, rutile phase is preferable to TiO₂ crystallite structure. As a result, when the temperature increases, anatase phase continuously transforms to rutile phase, which is more stable phase regarding crystallite size.

Table 5 Summary of crystallite structure of TiO₂ microfiber membrane (n=3)

Calcination temperature (°C)	Crystallite size (nm)		Anatase ratio
	Anatase	Rutile	
500	16.44±0.14	16.31±0.60	0.74±0.03
700	20.51±0.70	20.83±0.84	0.32±0.05

Figure 20 FESEM image of TiO₂ microfiber at calcination temperature of a) 500°C and b) 700°C

4.5 Gas sensing performance evaluation

The 700°C-annealed TiO₂ microfiber membrane are selected to minimize the effect of temperature on the crystallite structure of TiO₂ microfibers during gas sensing evaluation. TiO₂ microfiber membrane are successfully deposited on gold interdigitated electrode as shown in Figure 21.

Figure 21 FESEM image of TiO₂ microfiber membrane on gold-IDE

4.5.1 Temperature response of TiO₂ microfiber

The temperature response of TiO₂ microfiber membrane is shown in Figure 22. When the temperature increases from room temperature to 350°C, the resistance of sample decreases until reaching the minimum resistance of 0.4 GΩ at 350°C. The resistance of the sample increases again when the temperature returns to room temperature. The inverse proportion between resistance and temperature of TiO₂ microfiber is a normal property of semiconductor material. However, the first initial resistance value of the sample at room temperature is approximately 8.43 GΩ, while the second initial resistance at 30°C is approximately 35.3 GΩ, which is four times higher than the first initial value. This result should be due to the pre-absorption of conductive species such as moisture from the environment before the experiment. Hence, after conductive species are removed from the sample during the first temperature cycle, the resistance of the sample increases.

Figure 22 Temperature response from TiO₂ microfiber membrane on gold-IDE

4.5.2 Carbon monoxide gas response of TiO₂ microfibers

To demonstrate CO gas sensing performance of TiO₂ microfibers, the sample is heated up from room temperature to 350°C. As illustrated in Figure 23(a), when the temperature starts increasing to 100°C, the resistance of the sample continuously increases because the moisture inside TiO₂ microfibers start evaporating. The resistance of the sample continuously decreases until stabilizing at 350°C.

The average resistance of the sample at 350°C (R_{air}) is 6.40 GΩ ($n = 1800$, $\sigma_{air} = 1.24 \times 10^8$). The noise level of the reference resistance then can be calculated from this following equation

$$\text{noise level of baseline resistance} = \frac{3 \times \sigma_{air}}{R_{air}} = \frac{3 \times 1.24 \times 10^8}{6.40 \times 10^9} = 5.84 \times 10^{-2}$$

When sample is exposed to 200 ppm of CO gas, the resistance of the sample (R_{CO}) immediately decreases to 3.86 GΩ ($n = 1800$, $\sigma_{co} = 4.8 \times 10^8$) with the response time of 120 seconds as shown in Figure 23(b). Therefore, the sensitivity of the sample can be calculated as

$$\text{Sensitivity} = \frac{R_{air}}{R_{CO}} = \frac{6.40 \times 10^9}{3.86 \times 10^9} = 1.66$$

This decreasing of the resistance of TiO₂ microfiber membrane is due to the reduction properties of CO gas whereby giving electron to the TiO₂ microfiber surface. After removing CO gas from the testing chamber, the resistance of the sample returned to baseline level with the recovery time of 102 seconds.

The sensitivity of CO gas sensor in our study is lower than previous reports on TiO₂ microfiber [135-137], which could be due to several reasons. First, TiO₂ microfiber membrane is fabricated from the agglomeration of the TiN nanoparticles, while the other reports utilize the sol-gel method, which provide highly crystallite microfiber. Secondly, the distance of the interdigitated electrode is 100 μm, which lowers sensitivity of the sensors significantly. To improve the sensitivity, the distance between interdigitated electrode should be decreased.

Figure 23 CO gas response from TiO₂ microfiber membrane on gold IDE: a) the overall resistance response and b) the resistance response at 350 °C

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

We have successfully developed fabrication process and gas characterization system for high performance CO gas sensing TiO₂ microfiber membrane. The understanding in the effects of each parameter in the fabrication process is essential to customize TiO₂ microfiber membrane. As such, the diameter, the density, and the distribution of mesoporous TiO₂ microfiber can be adjusted by varying the electrospinning parameters. The ratio and size of crystalline TiO₂ can be controlled by adjusting temperature and duration in the thermal oxidation process. Therefore, the colloidal electrospinning of TiN-NPs in PVP combining with the thermal oxidation process is proven to be the potential candidate for the environmental-friendly mesoporous TiO₂ microfiber fabrication.

For the fabrication TiO₂ microfiber membrane for CO gas sensor, TiN-NPs are homogeneously dispersed in PVP solution at the concentration of 3%_{wt/v}. The uniform nonwoven TiN-NPs/PVP microfiber membranes are then deposited on gold-IDE. The electrospinning parameters of TiN-NPs/PVP colloidal solution are the flow rate of 1 ml/hour, the tip-to-collector distance of 15 cm, and the applying potential of 20 volts. Finally, TiN/PVP microfiber membranes are oxidized at 700°C for 2 hours. This fabrication procedure produces nonwoven mesoporous TiO₂ microfiber membrane with fiber diameters in the range of 200 – 700 nm. Owing to high thermal oxidation temperature, the crystallite structure of TiO₂ microfiber is dominated by rutile phase with the anatase ratio 0.32±0.05.

The custom-design gas sensor characterization system has been successfully established for CO gas sensor performance evaluation. The resistance of mesoporous TiO₂ microfiber membrane decreases from the initial resistance of 6.40 GΩ to the sensing resistance of 3.86 GΩ

upon exposing to CO gas concentration of 200 ppm at 350°C. The response and the recovery time of the sample are 120 seconds and 102 seconds respectively. These significant decreasing in resistance and fast response time result from the reduction of CO gas on the surface of TiO₂ couple with the large surface area of mesoporous microfiber membrane.

The successful fabrication and characterization of CO gas sensing mesoporous TiO₂ microfiber membrane provide both fundamental knowledge and skill in both environmental-friendly electrospinning process and gas sensor characterization system for fabricating high-performance gas sensing microfiber for personal protective equipment in the future.

5.2 Recommendations

This research project has built the basic microfiber fabrication and the gas characterization process. There are several improvements should be done in the future research.

First, since the current experiments has been focused on the fabrication and characterization setup, the sensitivity of CO gas sensing mesoporous TiO₂ microfiber membrane is still lower than the other reports [135-137]. Further investigations should be focused on the effect of distance between interdigitated electrode, the anatase ratio of TiO₂ microfiber, the operating temperature of the sensor, and the effect of moisture on the sensitivity of the sensors. In addition, as CO gas is the only gas that has been tested in this report, the selectivity of the sensor in the mixture of the other gases should be studied.

Secondly, besides maximizing the performance of gas sensing mesoporous TiO₂ microfiber membranes, the brittleness of TiO₂ microfibers and interdigitated electrode need to be overcome to achieve the gas sensing electronic textiles. As brittleness of TiO₂ microfibers is limited by the crystallite structure, the flexible chemiresistive materials such as conductive polymers should be investigated. The electrospinning of chemiresistive polymer such polypyrrole (PPy) or polyaniline (PANI) could potentially improve the stretchability and flexibility of the gas sensing element [33-35]. Moreover, the electrospinning of the composite metal oxides and conductive polymers could significantly improve the performance of the gas sensor [138, 142, 143, 146]. To initiate the study on the electrospinning of chemiresistive polymer, we attempted to electrospin polyaniline microfiber using our electrospinning setup as illustrated in Figure 24.

The concentration of PANI solution in this preliminary study was 20%_{w/v} PANI in PVP solution. The flow rate of the solution was 1 ml/hour, the tip-to-collector distance was 15 cm, and the apply potential is 25 kV. The gas sensing characteristic of this PANI microfiber membrane will be tested in the subsequent experiment. This study on chemiresistive polymer potentially lead to the composite TiO₂/PANI microfiber fabrication in the future.

Figure 24 FE-SEM images of PANI microfibers at magnification of a) 1k, b) 10k

Finally, flexible gas sensing microfibers should be deposited on the conductive fabrics or flexible electrodes as this project aims to create the futuristic personal protective equipment. The commercial interdigitated electrode on PET substrate in Figure 25 could be used to prove the possibility of flexible microfiber gas sensors.

Figure 25 Commercial PET interdigitated electrode

Publications

1. Thanit Apiwattanadej, Li Zhang, King Ho Holden Li, “*Electrospun polyurethane microfiber membrane on conductive textile for water-supported textile electrode in continuous ECG monitoring application*”, 19th edition of the symposium on Design, Test, Integration & Packaging of MEMS/MOEMS (DTIP), Rome, Italy (2018)
2. Thanit Apiwattanadej, Zhang Li, King Ho Holden Li, “*Embedding wearable sensors on textiles targeting aging populations based on breath able microfiber material suitable for tropical environment*”, 1st Ageing Research Institute for Society and Education Symposium (ARISE), Singapore (2017)
3. Thanit Apiwattanadej, Byung Jae Chun, Hyub Lee, King Ho Holden Li, Young-Jin Kim, “*Stability Test of the Silicon Fiber Bragg Grating Embroidered on Textile for Joint Angle Measurement*”, 5th International Conference on Optical and Photonic Engineering (ICOPEN2017), Singapore (2017)

References

- [1] E. O. Thorp, "The invention of the first wearable computer," in *Digest of Papers. Second International Symposium on Wearable Computers (Cat. No.98EX215)*, 1998, pp. 4-8.
- [2] S. Mann, "Wearable computing: a first step toward personal imaging," *Computer*, vol. 30, no. 2, pp. 25-32, 1997.
- [3] S. Mann, "Smart clothing: The wearable computer and wearcam," *Personal Technologies*, journal article vol. 1, no. 1, pp. 21-27, March 01 1997.
- [4] M. L. Hammock, A. Chortos, B. C. K. Tee, J. B. H. Tok, and Z. Bao, "25th Anniversary Article: The Evolution of Electronic Skin (E - Skin): A Brief History, Design Considerations, and Recent Progress," *Advanced Materials*, vol. 25, no. 42, pp. 5997-6038, 2013.
- [5] B. W. An, J. H. Shin, S.-Y. Kim, J. Kim, S. Ji, J. Park, Y. Lee, J. Jang, Y-G Park, and E. Cho, "Smart Sensor Systems for Wearable Electronic Devices," *Polymers*, vol. 9, no. 8, p. 303, 2017.
- [6] J. A. Rogers, T. Someya, and Y. Huang, "Materials and Mechanics for Stretchable Electronics," *Science*, vol. 327, no. 5973, pp. 1603-1607, 2010.
- [7] S. Wang, M. Li, J. Wu, D.-H. Kim, N. Lu, Y. Su, Z. Kang, Y. Huang, and J. A. Rogers, "Mechanics of epidermal electronics," *Journal of Applied Mechanics*, vol. 79, no. 3, p. 031022, 2012.
- [8] K.-I. Jang, S. Y. Han, S. Xu, K. E. Mathewson, Y. Zhang, J.-W. Jeong, G.-T. Kim, R. C. Webb, J. W. Lee, T. J. Dawidczyk, R. H. Kim, Y. M. Song, W.-H. Yeo, S. Kim, H. Cheng, S. L. Rhee, J. Chung, B. Kim, H. U. Chung, D. Lee, Y. Yang, M. Cho, J. G. Gaspar, R. Carbonari, M. Fabiani, G. Gratton, Y.

- Huang, and J. A. Rogers, "Rugged and breathable forms of stretchable electronics with adherent composite substrates for transcutaneous monitoring," *Nature Communications*, Article vol. 5, p. 4779, 2014.
- [9] Y. Chen, B. Lu, Y. Chen, and X. Feng, "Breathable and Stretchable Temperature Sensors Inspired by Skin," *Scientific Reports*, vol. 5, p. 11505, 2015.
- [10] B. Li, F. Zhang, S. Guan, J. Zheng, and C. Xu, "Wearable piezoelectric device assembled by one-step continuous electrospinning," *Journal of Materials Chemistry C*, 10.1039/C6TC01696K vol. 4, no. 29, pp. 6988-6995, 2016.
- [11] A. Miyamoto, S. Lee, N. F. Cooray, S. Lee, M. Mori, N. Matsuhisa, H. Jin, L. Yoda, T. Yokota, A. Itoh, M. Sekino, H. Kawasaki, T. Ebihara, M. Amagai, and T. Someya, "Inflammation-free, gas-permeable, lightweight, stretchable on-skin electronics with nanomeshes," *Nature Nanotechnology*, Article vol. 12, p. 907, 2017.
- [12] M. Weiser, "The computer for the 21st century," *SIGMOBILE Mob. Comput. Commun. Rev.*, vol. 3, no. 3, pp. 3-11, 1999.
- [13] J. Berzowska, "Electronic Textiles: Wearable Computers, Reactive Fashion, and Soft Computation," *TEXTILE*, vol. 3, no. 1, pp. 58-75, 2005.
- [14] L. Dunne, H. Profita, and C. Zeagler, "Chapter 1.2 - Social Aspects of Wearability and Interaction," in *Wearable Sensors* Oxford: Academic Press, 2014, pp. 25-43.
- [15] M. Ghahremani Honarvar and M. Latifi, "Overview of wearable electronics and smart textiles," *The Journal of The Textile Institute*, vol. 108, no. 4, pp. 631-652, 2017.
- [16] E. R. Post, M. Orth, P. Russo, and N. Gershenfeld, "E-broidery: Design and

- fabrication of textile-based computing," *IBM Systems journal*, vol. 39, no. 3.4, pp. 840-860, 2000.
- [17] S. Seymour, *Fashionable Technology. [electronic resource] : The Intersection of Design, Fashion, Science, and Technology*. Vienna : Springer Vienna, 2008.
 - [18] A. Schwarz and L. Van Langenhove, "2 - Types and processing of electro-conductive and semiconducting materials for smart textiles A2 - Kirstein, Tünde," in *Multidisciplinary Know-How for Smart-Textiles Developers*: Woodhead Publishing, 2013, pp. 29-69.
 - [19] X. Tao, V. Koncar, T.-H. Huang, C.-L. Shen, Y.-C. Ko, and G.-T. Jou, "How to Make Reliable, Washable, and Wearable Textronic Devices," *Sensors*, vol. 17, no. 4, p. 673, 2017.
 - [20] Y. Chen, D. W. Lloyd, and S. C. Harlock, "Mechanical Characteristics of Coated Fabrics," *The Journal of The Textile Institute*, vol. 86, no. 4, pp. 690-700, 1995.
 - [21] S. Farboodmanesh, J. Chen, J. L. Mead, K. D. White, H. E. Yesilalan, R. Laoulache, and S. B. Warner, "Effect of Coating Thickness and Penetration on Shear Behavior of Coated Fabrics," *Journal of Elastomers & Plastics*, vol. 37, no. 3, pp. 197-227, 2005.
 - [22] J. B. Pargana and V. M. A. Leitão, "A simplified stress–strain model for coated plain-weave fabrics used in Tensioned Fabric Structures," *Engineering Structures*, vol. 84, pp. 439-450, 2015.
 - [23] S. Lee, S. Shin, S. Lee, J. Seo, J. Lee, S. Son, H. J. Cho, H. Algadi, S. Al-Sayari, D.E. Kim, and T. Lee, "Ag Nanowire Reinforced Highly Stretchable Conductive Fibers for Wearable Electronics," *Advanced Functional*

- Materials*, vol. 25, no. 21, pp. 3114-3121, 2015.
- [24] S. Mi Yeon, K. Do Kyun, I. Kyo Jin, J. Seong Mu, and K. Dong Young, "Electrospun TiO_2 electrodes for dye-sensitized solar cells," *Nanotechnology*, vol. 15, no. 12, p. 1861, 2004.
- [25] W. Weng, P. Chen, S. He, X. Sun, and H. Peng, "Smart electronic textiles," *Angewandte Chemie International Edition*, vol. 55, no. 21, pp. 6140-6169, 2016.
- [26] A. Laforgue, G. Rouget, S. Dubost, M. F. Champagne, and L. Robitaille, "Multifunctional resistive-heating and color-changing monofilaments produced by a single-step coaxial melt-spinning process," *ACS Appl Mater Interfaces*, vol. 4, no. 6, pp. 3163-8, 2012.
- [27] C. J. Luo, S. D. Stoyanov, E. Stride, E. Pelan, and M. Edirisinghe, "Electrospinning versus fibre production methods: from specifics to technological convergence," *Chem Soc Rev*, vol. 41, no. 13, pp. 4708-35, 2012.
- [28] B. Ding, M. Wang, X. Wang, J. Yu, and G. Sun, "Electrospun nanomaterials for ultrasensitive sensors," *Materials Today*, vol. 13, no. 11, pp. 16-27, 2010.
- [29] A. Macagnano, E. Zampetti, and E. Kny, *Electrospinning for High Performance Sensors. [electronic resource]* (NanoScience and Technology). Cham : Springer International Publishing : Imprint: Springer, 2015.
- [30] R. Rajamanickam, S. Park, and S. Jayaraman, "A Structured Methodology for the Design and Development of Textile Structures in a Concurrent Engineering Framework," *The Journal of The Textile Institute*, vol. 89, no. 3, pp. 44-62, 1998.
- [31] S. Coyle, K. T. Lau, N. Moyna, D. O'Gorman, D. Diamond, F. D. Francesco,

- D. Costanzo, P. Salvo, M. G. Trivella, D. E. De Rossi, N. Taccini, R. Paradiso, J. A. Porchet, A. Ridolfi, J. Luprono, C. Chuzel, T. Lanier, F. Revol-Cavalier, S. Schoumacker, V. Mourier, I. Chartier, R. Convert, H. De-Moncuit, and C. Bini, "BIOTEX-Biosensing Textiles for Personalised Healthcare Management," *IEEE Transactions on Information Technology in Biomedicine*, vol. 14, no. 2, pp. 364-370, 2010.
- [32] D. Curone, E. L. Secco, A. Tognetti, G. Loriga, G. Dudnik, M. Risatti, R. Whyte, A. Bonfiglio, and G. Magenes, "Smart Garments for Emergency Operators: The ProeTEX Project," *IEEE Transactions on Information Technology in Biomedicine*, vol. 14, no. 3, pp. 694-701, 2010.
- [33] G. E. Collins and L. Buckley, "Conductive polymer-coated fabrics for chemical sensing," *Synthetic Metals*, vol. 78, no. 2, pp. 93-101, 1996.
- [34] X. Zhang, Z. Qin, X. Liu, B. Liang, N. Liu, Z. Zhou, and M. Zhu, "Flexible sensing fibers based on polyaniline-coated polyurethane for chloroform vapor detection," *Journal of Materials Chemistry A*, vol. 1, no. 35, pp. 10327-10333, 2013.
- [35] S. C. Deogaonkar and N. V. Bhat, "Polymer based fabrics as transducers in ammonia & ethanol gas sensing," *Fibers and Polymers*, journal article vol. 16, no. 8, pp. 1803-1811, 2015.
- [36] T. Seesaard, P. Lorwongtragool, and T. Kerdcharoen, "Development of fabric-based chemical gas sensors for use as wearable electronic noses," *Sensors*, vol. 15, no. 1, pp. 1885-1902, 2015.
- [37] Y. J. Yun, W. G. Hong, N.-J. Choi, B. H. Kim, Y. Jun, and H.-K. Lee, "Ultrasensitive and highly selective graphene-based single yarn for use in wearable gas sensor," *Scientific reports*, vol. 5, p. 10904, 2015.

- [38] Z. Gao, Z. Lou, S. Chen, L. Li, K. Jiang, Z. Fu, W. Han, and G. Shen, "Fiber gas sensor-integrated smart face mask for room-temperature distinguishing of target gases," *Nano Research*, journal article vol. 11, no. 1, pp. 511-519, 2018.
- [39] D. R. Miller, S. A. Akbar, and P. A. Morris, "Nanoscale metal oxide-based heterojunctions for gas sensing: A review," *Sensors and Actuators B: Chemical*, vol. 204, pp. 250-272, 2014.
- [40] S. Gupta Chatterjee, S. Chatterjee, A. K. Ray, and A. K. Chakraborty, "Graphene-metal oxide nanohybrids for toxic gas sensor: A review," *Sensors and Actuators B: Chemical*, vol. 221, pp. 1170-1181, 2015.
- [41] S. Park, K. Chung, and S. Jayaraman, "Chapter 1.1 - Wearables: Fundamentals, Advancements, and a Roadmap for the Future," in *Wearable Sensors* Oxford: Academic Press, 2014, pp. 1-23.
- [42] (2017, 19 February). *Gear S3*. Available: www.samsung.com/us/explore/gear-s3/
- [43] (2017, 19 February). *Apple Watch Series 3*. Available: www.apple.com/apple-watch-series-3/
- [44] (2017, 19 February). *Garmin*. Available: www.garmin.com
- [45] (2017, 19 February). *Fitbit*. Available: www.fitbit.com
- [46] (2017, 19 February). *Gear VR*. Available: www.samsung.com/global/galaxy/gear-vr/
- [47] (2017, 19 February). *Daydream*. Available: vr.google.com/daydream
- [48] (2017, 12 June). *iRhythm* Available: www.irhythmtech.com/
- [49] (2017, 22 February). *MC10*. Available: www.mc10inc.com
- [50] S. Yoshimoto, T. Araki, T. Uemura, T. Nezu, M. Kondo, K. Sasai, M. Iwase,

- H. Satake, A. Yoshida, M. Kikuchi, and T. Sekitani, "Wireless EEG patch sensor on forehead using on-demand stretchable electrode sheet and electrode-tissue impedance scanner," in *2016 38th Annual International Conference of the IEEE Engineering in Medicine and Biology Society (EMBC)*, 2016, pp. 6286-6289.
- [51] S. Khan, L. Lorenzelli, and R. S. Dahiya, "Technologies for Printing Sensors and Electronics Over Large Flexible Substrates: A Review," *IEEE Sensors Journal*, vol. 15, no. 6, pp. 3164-3185, 2015.
- [52] R. Das, "Printed, Flexible and Hybrid Electronics: Hot Trends and Market Outlook," IDTechEx2017, Available: <https://www.idtechex.com/research/webinars/printed-flexible-and-hybrid-electronics-hot-trends-and-market-outlook-00105.asp>.
- [53] M. Stoppa and A. Chiolerio, "Wearable electronics and smart textiles: a critical review," *Sensors (Basel)*, vol. 14, no. 7, pp. 11957-92, 2014.
- [54] (2017, 27 June). *Athos*. Available: www.liveathos.com
- [55] (2017, 27 June). *Hexoskin*. Available: www.hexoskin.com
- [56] (26 June). *Bloomer Bra*. Available: www.bloomertech.com
- [57] (12 June). *Sensoria fitness*. Available: <http://www.sensoriafitness.com/technology>
- [58] (2017, 27 June). *Levi commuter x google jacquard*. Available: www.levi.com/US/en_US/features/levi-commuter-xgoogle-jacquard/
- [59] J. Hayward. (2017, 21 June). *E-textiles 2017-2027: Technologies, Markets, Players*. Available: <http://www.idtechex.com/research/reports/e-textiles-2017-2027-technologies-markets-players-000522.asp>
- [60] M. Orth, "Defining Flexibility and Sewability in Conductive Yarns," *MRS*

Proceedings, vol. 736, p. D1.4, 2011, Art. no. D1.4.

- [61] S. Anne, K. Lida, C. Laetitia, H. Carla, G. Filip, C. Geert De, and L. Lieva Van, "Comparative study on the mechanical properties of elastic, electro-conductive hybrid yarns and their input materials," *Textile Research Journal*, vol. 81, no. 16, pp. 1713-1723, 2011.
- [62] I. Poupyrev, N.-W. Gong, S. Fukuhara, M. E. Karagozler, C. Schwesig, and K. E. Robinson, "Project Jacquard: Interactive Digital Textiles at Scale," presented at the Proceedings of the 2016 CHI Conference on Human Factors in Computing Systems, Santa Clara, California, USA, 2016.
- [63] T. Linz, E. P. Simon, and H. Walter, "Modeling embroidered contacts for electronics in textiles," *The Journal of The Textile Institute*, vol. 103, no. 6, pp. 644-653, 2012.
- [64] T. Linz, C. Kallmayer, R. Aschenbrenner, and H. Reichl, "Fully untegrated EKG shirt based on embroidered electrical interconnections with conductive yarn and miniaturized flexible electronics," in *International Workshop on Wearable and Implantable Body Sensor Networks (BSN'06)*, 2006, pp. 4 pp.-26.
- [65] T. Vervust, G. Buyle, F. Bossuyt, and J. Vanfleteren, "Integration of stretchable and washable electronic modules for smart textile applications," *The Journal of The Textile Institute*, vol. 103, no. 10, pp. 1127-1138, 2012.
- [66] L. M. Castano and A. B. Flatau, "Smart fabric sensors and e-textile technologies: a review," *Smart Materials and Structures*, vol. 23, no. 5, p. 053001, 2014.
- [67] K. Jost, G. Dion, and Y. Gogotsi, "Textile energy storage in perspective," *Journal of Materials Chemistry A*, 10.1039/C4TA00203B vol. 2, no. 28, pp.

10776-10787, 2014.

- [68] S. Zhai, H. E. Karahan, L. Wei, Q. Qian, A. T. Harris, A. I. Minett, S. Ramakrishna, A. K. Ng, and Y. Chen, "Textile energy storage: Structural design concepts, material selection and future perspectives," *Energy Storage Materials*, vol. 3, pp. 123-139, 2016.
- [69] K. K. Chawla, *Fibrous Materials. [electronic resource]* (Cambridge Solid State Science Series). Cambridge : Cambridge University Press, 1998, 2005.
- [70] F. Ullmann, *Ullmann's fibers*. Weinheim : Wiley-VCH, c2008., 2008.
- [71] (2017, 13 March). *Large area processing*. Available: <https://www.a-star.edu.sg/simtech/LAP/About-Large-Area-Processing>
- [72] (2017, 13 March). *Printed Electronics*. Available: <http://emsadhesives.com/products/printed-electronics/>
- [73] S. Merilampi, T. Laine-Ma, and P. Ruuskanen, "The characterization of electrically conductive silver ink patterns on flexible substrates," *Microelectronics Reliability*, vol. 49, no. 7, pp. 782-790, 2009.
- [74] N. Matsuhisa, M. Kaltenbrunner, T. Yokota, H. Jinno, K. Kuribara, T. Sekitani, and T. Someya, "Printable elastic conductors with a high conductivity for electronic textile applications," *Nature Communications*, Article vol. 6, p. 7461, 2015.
- [75] H. Kim, Y. Kim, Y. S. Kwon, and H. J. Yoo, "A 1.12mW Continuous Healthcare Monitor Chip Integrated on a Planar Fashionable Circuit Board," in *2008 IEEE International Solid-State Circuits Conference - Digest of Technical Papers*, 2008, pp. 150-603.
- [76] Y. Kim, H. Kim, and H. J. Yoo, "Electrical Characterization of Screen-Printed Circuits on the Fabric," *IEEE Transactions on Advanced Packaging*,

vol. 33, no. 1, pp. 196-205, 2010.

- [77] H. Kim, Y. Kim, B. Kim, and H. J. Yoo, "A Wearable Fabric Computer by Planar-Fashionable Circuit Board Technique," in *2009 Sixth International Workshop on Wearable and Implantable Body Sensor Networks*, 2009, pp. 282-285.
- [78] H. J. Yoo, J. Yoo, and L. Yan, "Wireless fabric patch sensors for wearable healthcare," in *2010 Annual International Conference of the IEEE Engineering in Medicine and Biology*, 2010, pp. 5254-5257.
- [79] S. Lee, B. Kim, and H.-J. Yoo, *Planar Fashionable Circuit Board Technology and Its Applications*. 2009.
- [80] X. Fan, Z. Z. Chu, F. Z. Wang, C. Zhang, L. Chen, Y. W. Tang, and D. C. Zou, "Wire-Shaped Flexible Dye-sensitized Solar Cells," *Advanced Materials*, vol. 20, no. 3, pp. 592-595, 2008.
- [81] Y. Zhang, W. Bai, X. Cheng, J. Ren, W. Weng, P. Chen, X. Fang, Z. Zhang, and H. Peng, "Flexible and stretchable lithium-ion batteries and supercapacitors based on electrically conducting carbon nanotube fiber springs," *Angew Chem Int Ed Engl*, vol. 53, no. 52, pp. 14564-8, Dec 22 2014.
- [82] L. Qiu, J. Deng, X. Lu, Z. Yang, and H. Peng, "Integrating perovskite solar cells into a flexible fiber," *Angew Chem Int Ed Engl*, vol. 53, no. 39, pp. 10425-8, 2014.
- [83] Y. Qin, X. Wang, and Z. L. Wang, "Microfibre-nanowire hybrid structure for energy scavenging," *Nature*, vol. 451, no. 7180, pp. 809-13, 2008.
- [84] X. Sheng, Q. Yong, X. Chen, W. Yaguang, Y. Rusen, and W. Zhong Lin, "Self-powered nanowire devices," *Nature Nanotechnology*, Article vol. 5, no. 5, pp. 366-373, 2010.

- [85] J. H. Wendorff, S. P. Agarwal, and A. Greiner, *Electrospinning. [electronic resource] : materials, processing, and applications*. Weinheim ; Hoboken, N.J. : John Wiley & Sons, 2012., 2012.
- [86] A. L. Yarin, S. Koombhongse, and D. H. Reneker, "Taylor cone and jetting from liquid droplets in electrospinning of nanofibers," *Journal of applied physics*, vol. 90, no. 9, pp. 4836-4846, 2001.
- [87] M. M. Hohman, M. Shin, G. Rutledge, and M. P. Brenner, "Electrospinning and electrically forced jets. II. Applications," *Physics of fluids*, vol. 13, no. 8, pp. 2221-2236, 2001.
- [88] D. H. Reneker, A. L. Yarin, H. Fong, and S. Koombhongse, "Bending instability of electrically charged liquid jets of polymer solutions in electrospinning," *Journal of Applied physics*, vol. 87, no. 9, pp. 4531-4547, 2000.
- [89] M. M. Hohman, M. Shin, G. Rutledge, and M. P. Brenner, "Electrospinning and electrically forced jets. I. Stability theory," *Physics of fluids*, vol. 13, no. 8, pp. 2201-2220, 2001.
- [90] Y. M. Shin, M. M. Hohman, M. P. Brenner, and G. C. Rutledge, "Experimental characterization of electrospinning: the electrically forced jet and instabilities," *Polymer*, vol. 42, no. 25, pp. 09955-09967, 2001.
- [91] D. H. Reneker, A. L. Yarin, E. Zussman, and H. Xu, "Electrospinning of Nanofibers from Polymer Solutions and Melts," in *Advances in Applied Mechanics*, vol. 41, H. Aref and E. van der Giessen, Eds.: Elsevier, 2007, pp. 43-346.
- [92] D. H. Reneker and A. L. Yarin, "Electrospinning jets and polymer nanofibers," *Polymer*, vol. 49, no. 10, pp. 2387-2425, 2008.

- [93] G. Taylor, "Disintegration of water drops in an electric field," *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, vol. 280, no. 1382, pp. 383-397, 1964.
- [94] D. Zhang and J. Chang, "Patterning of Electrospun Fibers Using Electroconductive Templates," *Advanced Materials*, vol. 19, no. 21, pp. 3664-3667, 2007.
- [95] S. J. Cho, B. Kim, T. An, and G. Lim, "Replicable Multilayered Nanofibrous Patterns on a Flexible Film," *Langmuir*, vol. 26, no. 18, pp. 14395-14399, 2010.
- [96] J. Lee, S. Y. Lee, J. Jang, Y. H. Jeong, and D.-W. Cho, "Fabrication of Patterned Nanofibrous Mats Using Direct-Write Electrospinning," *Langmuir*, vol. 28, no. 18, pp. 7267-7275, 2012.
- [97] A. K. Haghi, *Electrospinning of nanofibers in textiles*. Toronto : Apple Academic Press, c2012., 2012.
- [98] S. R. Coles and A. Wooldridge, "Chapter 4 Optimising Solutions for Electrospinning," in *Electrospinning: Principles, Practice and Possibilities*: The Royal Society of Chemistry, 2015, pp. 57-70.
- [99] F. J. Davis, S. D. Mohan, and M. A. Ibraheem, "Chapter 1 Introduction," in *Electrospinning: Principles, Practice and Possibilities*: The Royal Society of Chemistry, 2015, pp. 1-21.
- [100] W. E. Teo and S. Ramakrishna, "A review on electrospinning design and nanofibre assemblies," *Nanotechnology*, vol. 17, no. 14, p. R89, 2006.
- [101] C. J. Angammana and S. H. Jayaram, "Fundamentals of electrospinning and processing technologies," *Particulate Science and Technology*, vol. 34, no. 1, pp. 72-82, 2016.

- [102] X. Yan, J. Marini, R. Mulligan, A. Deleault, U. Sharma, M. P. Brenner, G. C. Rutledge, T. Freyman, and Q. P. Pham, "Slit-surface electrospinning: a novel process developed for high-throughput fabrication of core-sheath fibers," *PLoS One*, vol. 10, no. 5, p. e0125407, 2015.
- [103] A. Mirabedini, J. Foroughi, and G. G. Wallace, "Developments in conducting polymer fibres: from established spinning methods toward advanced applications," *RSC Advances*, 10.1039/C6RA05626A vol. 6, no. 50, pp. 44687-44716, 2016.
- [104] M. Bognitzki, M. Becker, M. Graeser, W. Massa, J. H. Wendorff, A. Schaper, D. Weber, A. Beyer, A. Götzhäuser, and A. Greiner, "Preparation of Sub - micrometer Copper Fibers via Electrospinning," *Advanced Materials*, vol. 18, no. 18, pp. 2384-2386, 2006.
- [105] H. Wu, R. Zhang, X. Liu, D. Lin, and W. Pan, "Electrospinning of Fe, Co, and Ni Nanofibers: Synthesis, Assembly, and Magnetic Properties," *Chemistry of Materials*, vol. 19, no. 14, pp. 3506-3511, 2007.
- [106] E. Zussman, A. L. Yarin, A. V. Bazilevsky, R. Avrami, and M. Feldman, "Electrospun Polyaniline/Poly(methyl methacrylate) - Derived Turbostratic Carbon Micro - /Nanotubes," *Advanced Materials*, vol. 18, no. 3, pp. 348-353, 2006.
- [107] J. Laudenslager Michael, H. Scheffler Raymond, and M. Sigmund Wolfgang, "Electrospun materials for energy harvesting, conversion, and storage: A review," in *Pure and Applied Chemistry* vol. 82, ed, 2010, p. 2137.
- [108] D. Joly, J.-W. Jung, I.-D. Kim, and R. Demadrille, "Electrospun materials for solar energy conversion: innovations and trends," *Journal of Materials Chemistry C*, 10.1039/C6TC00702C vol. 4, no. 43, pp. 10173-10197, 2016.

- [109] W. D. Jr. (2017, 26 June). *BLAST: Greater Speed, Accuracy in Recognizing Brain Injury*. Available: <https://www.onr.navy.mil/Media-Center/Press-Releases/2017/ONR-BLAST-TBI-Protection.aspx>
- [110] (2018, 6 February). *Air pollution*. Available: <http://www.who.int/airpollution/en/>
- [111] H. Jane and P. T. Ralph, "Optical gas sensing: a review," *Measurement Science and Technology*, vol. 24, no. 1, p. 012004, 2013.
- [112] E. Bakker and M. Telting-Diaz, "Electrochemical Sensors," *Analytical Chemistry*, vol. 74, no. 12, pp. 2781-2800, 2002.
- [113] D. K. Aswal and S. K. Gupta, *Science and technology of chemiresistor gas sensors*. New York : Nova Science Publishers, c2007., 2007.
- [114] H. Park, H. Ahn, D.-J. Kim, and H. Koo, "Nanostructured gas sensors integrated into fabric for wearable breath monitoring system," in *Proceedings of the 2013 International Symposium on Wearable Computers*, 2013, pp. 129-130: ACM.
- [115] B. Ding, M. Wang, J. Yu, and G. Sun, "Gas Sensors Based on Electrospun Nanofibers," *Sensors (Basel, Switzerland)*, vol. 9, no. 3, pp. 1609-1624, 2009.
- [116] D. Li and Y. Xia, "Fabrication of Titania Nanofibers by Electrospinning," *Nano Letters*, vol. 3, no. 4, pp. 555-560, 2003.
- [117] E. Formo, E. Lee, D. Campbell, and Y. Xia, "Functionalization of Electrospun TiO₂ Nanofibers with Pt Nanoparticles and Nanowires for Catalytic Applications," *Nano Letters*, vol. 8, no. 2, pp. 668-672, 2008.
- [118] Q. Li, D. J. G. Satur, H. Kim, and H. G. Kim, "Preparation of sol-gel modified electrospun TiO₂ nanofibers for improved photocatalytic decomposition of ethylene," (in English), *Materials Letters*, Article vol. 76,

pp. 169-172, 2012.

- [119] J. Y. Park, J. H. Lee, D. Y. Choi, J. W. Lee, and C. H. Hwang, "Influence of Fe doping on phase transformation and crystallite growth of electrospun TiO₂ nanofibers for photocatalytic reaction," (in English), *Materials Letters*, Article vol. 88, pp. 156-159, 2012.
- [120] D. Y. Choi, C. H. Hwang, I. H. Lee, I. H. Oh, J. W. Lee, and J. Y. Park, "Characterization of TiO₂ fibers by combined electrospinning method and hydrothermal reaction," (in English), *Materials Letters*, Article vol. 106, pp. 41-44, 2013.
- [121] H. R. Pant, B. Pant, P. Pokharel, H. J. Kim, L. D. Tijing, C. H. Park, D. S. Lee, H. Y. Kim, and C. S. Kim, "Photocatalytic TiO₂-RGO/nylon-6 spider-wave-like nano-nets via electrospinning and hydrothermal treatment," *Journal of Membrane Science*, Article vol. 429, pp. 225-234, 2013.
- [122] H. R. Pant, S. P. Adhikari, B. Pant, M. K. Joshi, H. J. Kim, C. H. Park, and C. S. Kim, "Immobilization of TiO₂ nanofibers on reduced graphene sheets: Novel strategy in electrospinning," *Journal of Colloid And Interface Science*, Article vol. 457, pp. 174-179, 2015.
- [123] R. Sedghi, H. R. Moazzami, S. S. Hosseiny Davarani, M. R. Nabid, and A. R. Keshtkar, "A one step electrospinning process for the preparation of polyaniline modified TiO₂/polyacrylonitrile nanocomposite with enhanced photocatalytic activity," *Journal of Alloys and Compounds*, Article vol. 695, pp. 1073-1079, 2017.
- [124] Q. Tang, X. Meng, Z. Wang, J. Zhou, and H. Tang, "One-step electrospinning synthesis of TiO₂/g-C₃N₄ nanofibers with enhanced photocatalytic properties," (in English), *Applied Surface Science*, Article vol. 430, pp. 253-

262, 02 / 01 / 2018.

- [125] S. Zhan, D. Chen, X. Jiao, and C. Tao, "Long TiO₂ Hollow Fibers with Mesoporous Walls: Sol–Gel Combined Electrospun Fabrication and Photocatalytic Properties," *The Journal of Physical Chemistry B*, vol. 110, no. 23, pp. 11199-11204, 2006.
- [126] O. Katsuhiro, D. Bin, T. Yosuke, N. Takayuki, Y. Michiyo, S. Shinichiro, O. Shingo, Y. Masato, and S. Seimei, "Electrospinning processed nanofibrous TiO₂ membranes for photovoltaic applications," *Nanotechnology*, vol. 17, no. 4, p. 1026, 2006.
- [127] S. K. Choi, S. Kim, S. K. Lim, and H. Park, "Photocatalytic Comparison of TiO₂ Nanoparticles and Electrospun TiO₂ Nanofibers: Effects of Mesoporosity and Interparticle Charge Transfer," *The Journal of Physical Chemistry C*, vol. 114, no. 39, pp. 16475-16480, 2010.
- [128] S. K. Choi, S. Kim, J. Ryu, S. K. Lim, and H. Park, "Titania nanofibers as a photo-antenna for dye-sensitized solar hydrogen," *Photochemical & Photobiological Sciences*, 10.1039/C2PP25054C vol. 11, no. 9, pp. 1437-1444, 2012.
- [129] R. Asmatulu, M. Ceylan, and N. Nuraje, "Study of Superhydrophobic Electrospun Nanocomposite Fibers for Energy Systems," *Langmuir*, vol. 27, no. 2, pp. 504-507, 2011.
- [130] Z. Li, H. Zhang, W. Zheng, W. Wang, H. Huang, C. Wang, A. G. MacDiarmid, and Wei Yen, "Highly Sensitive and Stable Humidity Nanosensors Based on LiCl Doped TiO₂ Electrospun Nanofibers," *Journal of the American Chemical Society*, vol. 130, no. 15, pp. 5036-5037, 2008.
- [131] H. Zhang, Z. Li, L. Liu, C. Wang, Y. Wei, and A. G. MacDiarmid,

- "Mg²⁺/Na⁺-doped rutile TiO₂ nanofiber mats for high-speed and anti-fogged humidity sensors," *Talanta*, vol. 79, no. 3, pp. 953-958, 2009.
- [132] X.-J. Yue, T.-S. Hong, X. Xu, and Z. Li, "High-Performance Humidity Sensors Based on Double-Layer ZnO-TiO₂ Nanofibers via Electrospinning," *Chinese Physics Letters*, vol. 28, no. 9, p. 090701, 2011.
- [133] H. Jamil, S. S. Batool, Z. Imran, M. Usman, M. A. Rafiq, M. Willander, and M. M. Hassan, "Electrospun titanium dioxide nanofiber humidity sensors with high sensitivity," *Ceramics International*, vol. 38, no. 3, pp. 2437-2441, 2012.
- [134] M. Su, J. Wang, H. Du, P. Yao, Y. Zheng, and X. Li, "Characterization and humidity sensitivity of electrospun ZrO₂:TiO₂ hetero-nanofibers with double jets," *Sensors and Actuators B: Chemical*, vol. 161, no. 1, pp. 1038-1045, 2012.
- [135] L. Osnat, R. Avner, and Z. Eyal, "Processing-Microstructure-Properties Correlation of Ultrasensitive Gas Sensors Produced by Electrospinning," *Chemistry of Materials*, Article vol. 21, no. 1, pp. 9-11, 2009.
- [136] J.-A. Park, J. Moon, S.-J. Lee, S. H. Kim, T. Zyung, and H. Y. Chu, "Structure and CO gas sensing properties of electrospun TiO₂ nanofibers," *Materials Letters*, Article vol. 64, no. 3, pp. 255-257, 2010.
- [137] J. Zhang, S.-W. Choi, and S. S. Kim, "Micro- and nano-scale hollow TiO₂ fibers by coaxial electrospinning: Preparation and gas sensing," *Journal of Solid State Chemistry*, Article vol. 184, pp. 3008-3013, 2011.
- [138] S. H. Nimkar, S. P. Agrawal, and S. B. Kondawar, "Fabrication of Electrospun Nanofibers of Titanium Dioxide Intercalated Polyaniline Nanocomposites for CO₂ Gas Sensor," *Procedia Materials Science*, vol. 10,

pp. 572-579, 2015/01/01/ 2015.

- [139] J. Yun, H.-I. Kim, and Y.-S. Lee, "A hybrid gas-sensing material based on porous carbon fibers and a TiO photocatalyst," *Journal of Materials Science*, Article vol. 48, no. 23, pp. 8320-8328, 2013.
- [140] I.-D. Kim, A. Rothschild, B. H. Lee, D. Y. Kim, S. M. Jo, and H. L. Tuller, "Ultrasensitive Chemiresistors Based on Electrospun TiO₂ Nanofibers," *Nano Letters*, vol. 6, no. 9, pp. 2009-2013, 2006.
- [141] J. Moon, J. A. Park, S. J. Lee, T. Zyung, and I. D. Kim, "Pd-doped TiO₂ nanofiber networks for gas sensor applications," (in English), *Sensors and Actuators, B: Chemical*, Article vol. 149, no. 1, pp. 301-305, 2010.
- [142] E. Zampetti, S. Pantalei, A. Muzyczuk, A. Bearzotti, F. De Cesare, C. Spinella, and A. Macagnano, "A high sensitive NO₂ gas sensor based on PEDOT–PSS/TiO₂ nanofibres," *Sensors & Actuators: B. Chemical*, Article vol. 176, pp. 390-398, 2013.
- [143] J. Gong, Y. Li, Z. Hu, Z. Zhou, and Y. Deng, "Ultrasensitive NH₃ gas sensor from polyaniline nanograin enched TiO₂ fibers," (in English), *Journal of Physical Chemistry C*, Article vol. 114, no. 21, pp. 9970-9974, 06 / 03 / 2010.
- [144] Y. Al-Hadeethi, A. Umar, A. A. Ibrahim, S. H. Al-Heniti, R. Kumar, S. Baskoutas, and B. M. Raffah, "Synthesis, characterization and acetone gas sensing applications of Ag-doped ZnO nanoneedles," *Ceramics International*, vol. 43, no. 9, pp. 6765-6770, 2015.
- [145] Y. Zheng, J. Wang, P. Chen, C. Li, and X. Li, "Structure and Gas-Sensing Behavior of Electrospun Titania-Doped Chromium Oxide Fibers," *International Journal of Applied Ceramic Technology*, vol. 10, pp. E304-E309, 2013.

- [146] Z. Pang, Q. Nie, P. Lv, J. Yu, F. Huang, and Q. Wei, "- Design of flexible PANI-coated CuO-TiO₂-SiO₂ heterostructure nanofibers with high ammonia sensing response values," vol. - 28, no. - 22, 2014.
- [147] W. Sigmund, J. Yuh, H. Park, V. Maneeratana, G. Pyrgiotakis, A. Daga, J. Taylor, and J. C. Nino, "Processing and Structure Relationships in Electrospinning of Ceramic Fiber Systems," *Journal of the American Ceramic Society*, vol. 89, no. 2, pp. 395-407, 2006.
- [148] D. Crespy, "Chapter 7 Electrospinning of Nanoparticles," in *Electrospinning: Principles, Practice and Possibilities*: The Royal Society of Chemistry, 2015, pp. 121-135.
- [149] S. Agarwal and A. Greiner, "On the way to clean and safe electrospinning—green electrospinning: emulsion and suspension electrospinning," *Polymers for Advanced Technologies*, vol. 22, no. 3, pp. 372-378, 2011.
- [150] D. Crespy, K. Friedemann, and A. M. Popa, "Colloid - Electrospinning: Fabrication of Multicompartment Nanofibers by the Electrospinning of Organic or/and Inorganic Dispersions and Emulsions," *Macromolecular Rapid Communications*, vol. 33, no. 23, pp. 1978-1995, 2012.
- [151] W. Schwarz, *PVP: a critical review of the kinetics and toxicology of polyvinylpyrrolidone (povidone)*. CRC Press, 1990.
- [152] T. Z. Yuan, "Electrospinning of nanofiber for tissue engineering," Nanyang Technological University 2017.
- [153] H. R. Pant, M. P. Bajgai, K. T. Nam, Y. A. Seo, D. R. Pandeya, S. T. Hong, and H. Y. Kim, "Electrospun nylon-6 spider-net like nanofiber mat containing TiO₂ nanoparticles: A multifunctional nanocomposite textile material," *Journal of Hazardous Materials*, Article vol. 185, pp. 124-130,

2011.

- [154] H. R. Pant, D. R. Pandeya, K. T. Nam, W.-i. Baek, S. T. Hong, and H. Y. Kim, "Photocatalytic and antibacterial properties of a TiO₂/nylon-6 electrospun nanocomposite mat containing silver nanoparticles," *Journal of Hazardous Materials*, Article vol. 189, pp. 465-471, 2011.
- [155] J. H. Kim, H. J. Kim, N. J. Choi, C. S. Kim, H. R. Pant, and J. H. Kim, "- Fabrication of multifunctional TiO₂-fly ash/polyurethane nanocomposite membrane via electrospinning," vol.40, no.2, pp.3029, 2014.
- [156] Q. Zhu, X. Li, Z. Fan, Y. Xu, H. Niu, C. Li, Y. Dang, Z. Huang, Y. Wang, and J. Guan, "Biomimetic polyurethane/TiO₂ nanocomposite scaffolds capable of promoting biomineralization and mesenchymal stem cell proliferation," *Materials Science & Engineering C*, Article vol. 85, pp. 79-87, 2018.
- [157] B. Wang, Z. Chen, J. Zhang, J. Cao, S. Wang, Q. Tian, M. Gao, and Q. Xu, "Fabrication of PVA/graphene oxide/TiO₂ composite nanofibers through electrospinning and interface sol–gel reaction: Effect of graphene oxide on PVA nanofibers and growth of TiO₂," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Article vol. 457, pp. 318-325, 2014.
- [158] Z. Guo, J. Xiong, M. Yang, S. Xiong, J. Chen, Y. Wu, H. Fan, L. Sun, J. Wang, and H. Wang, "Dispersion of nano-TiN powder in aqueous media," *Journal of Alloys and Compounds*, vol. 493, no. 1, pp. 362-367, 2010.
- [159] J. Xiong, S. Xiong, Z. Guo, M. Yang, J. Chen, and H. Fan, "Ultrasonic dispersion of nano TiC powders aided by Tween 80 addition," *Ceramics International*, vol. 38, no. 3, pp. 1815-1821, 2012.
- [160] C. A. Schneider, W. S. Rasband, and K. W. Eliceiri, "NIH Image to ImageJ:

- 25 years of image analysis," *Nat Meth*, 10.1038/nmeth.2089 vol. 9, no. 7, pp. 671-675, 2012.
- [161] N. A. Hotaling, K. Bharti, H. Kriel, and C. G. Simon, "DiameterJ: A validated open source nanofiber diameter measurement tool," *Biomaterials*, vol. 61, pp. 327-338, 2015.
- [162] H. P. Klug and L. E. Alexander, *X-ray diffraction procedures for polycrystalline and amorphous materials*. New York : Wiley, [1974] 2d ed., 1974.
- [163] R. A. Spurr and H. Myers, "Quantitative Analysis of Anatase-Rutile Mixtures with an X-Ray Diffractometer," *Analytical Chemistry*, vol. 29, no. 5, pp. 760-762, 1957.
- [164] M. M. Arafat, B. Dinan, S. A. Akbar, and A. S. M. A. Haseeb, "Gas Sensors Based on One Dimensional Nanostructured Metal-Oxides: A Review," *Sensors*, vol. 12, no. 6, p. 7207, 2012.
- [165] G. L. Hornyak, *Introduction to nanoscience*. Boca Raton : CRC Press, c2008., 2008.
- [166] J.-Y. Park, I.-H. Lee, and J.-J. Yun, "Influence of silver doping on the phase transformation and crystallite growth of electrospun TiO₂ nanofibers," 2010.
- [167] M. Hu, M. Fang, C. Tang, T. Yang, Z. Huang, Y. Liu, X. Wu, and X. Min, "The effects of atmosphere and calcined temperature on photocatalytic activity of TiO₂ nanofibers prepared by electrospinning," *Nanoscale Research Letters*, journal article vol. 8, no. 1, p. 548, 2013.
- [168] F. Zhang, Z. Cheng, L. Cui, T. Duan, A. Anan, C. Zhang, and L. Kang, "Controllable synthesis of Ag/TiO₂ heterostructures with enhanced photocatalytic activities under UV and visible excitation," *RSC Advances*,

- 10.1039/C5RA17762F vol. 6, no. 3, pp. 1844-1850, 2016.
- [169] N. C. Saha and H. G. Tompkins, "Titanium nitride oxidation chemistry: An x - ray photoelectron spectroscopy study," *Journal of Applied Physics*, vol. 72, no. 7, pp. 3072-3079, 1992.
- [170] T. Morikawa, R. Asahi, T. Ohwaki, K. Aoki, and Y. Taga, "Band-gap narrowing of titanium dioxide by nitrogen doping," *Japanese Journal of Applied Physics*, vol. 40, no. 6A, p. L561, 2001.
- [171] Z. Wu, F. Dong, W. Zhao, and S. Guo, "Visible light induced electron transfer process over nitrogen doped TiO₂ nanocrystals prepared by oxidation of titanium nitride," *Journal of Hazardous Materials*, vol. 157, no. 1, pp. 57-63, 2008.
- [172] H. Xin - Mei, H. Xiao - Jun, and C. Kuo - Chih, "Kinetics of Thermal Oxidation of Titanium Nitride Powder at Different Oxidizing Atmospheres," *Journal of the American Ceramic Society*, vol. 94, no. 2, pp. 570-575, 2011.
- [173] Y. Yang, X. Ji, M. Jing, H. Hou, Y. Zhu, L. Fang, X. Yang, Q. Chen, and C. E. Banks, "Carbon dots supported upon N-doped TiO₂ nanorods applied into sodium and lithium ion batteries," *Journal of Materials Chemistry A*, 10.1039/C4TA05611F vol. 3, no. 10, pp. 5648-5655, 2015.
- [174] A. Abbasi and J. Jahanbin Sardroodi, "N-doped TiO₂ anatase nanoparticles as a highly sensitive gas sensor for NO₂ detection: insights from DFT computations," *Environmental Science: Nano*, 10.1039/C6EN00159A vol. 3, no. 5, pp. 1153-1164, 2016.
- [175] A. Abbasi and J. Jahanbin Sardroodi, "Modified N-doped TiO₂ anatase nanoparticle as an ideal O₃ gas sensor: Insights from density functional theory calculations," *Computational and Theoretical Chemistry*, vol. 1095,

pp. 15-28, 2016.

- [176] Y.-F. Chen, C.-Y. Lee, M.-Y. Yeng, and H.-T. Chiu, "The effect of calcination temperature on the crystallinity of TiO₂ nanopowders," *Journal of Crystal Growth*, vol. 247, no. 3, pp. 363-370, 2003.
- [177] A. Kumar, R. Jose, K. Fujihara, J. Wang, and S. Ramakrishna, "Structural and Optical Properties of Electrospun TiO₂ Nanofibers," *Chemistry of Materials*, vol. 19, no. 26, pp. 6536-6542, 2007.
- [178] L. Wan, J. F. Li, J. Y. Feng, W. Sun, and Z. Q. Mao, "Improved optical response and photocatalysis for N-doped titanium oxide (TiO₂) films prepared by oxidation of TiN," *Applied Surface Science*, vol. 253, no. 10, pp. 4764-4767, 2007.
- [179] M. V. Diamanti, S. Codeluppi, A. Cordioli, and M. P. Pedferri, "Effect of thermal oxidation on titanium oxides' characteristics," *Journal of Experimental Nanoscience*, vol. 4, no. 4, pp. 365-372, 2009.
- [180] K. Zakrzewska and M. Radecka, "TiO₂-Based Nanomaterials for Gas Sensing—Influence of Anatase and Rutile Contributions," *Nanoscale Research Letters*, vol. 12, p. 89, 2017.
- [181] A. S. Bakri, M. Z. Sahdan, F. Adriyanto, N. A. Raship, N. D. M. Said, S. A. Abdullah, and M. S. Rahim, "Effect of annealing temperature of titanium dioxide thin films on structural and electrical properties," in *AIP Conference Proceedings*, 2017, vol. 1788, no. 1, p. 030030: AIP Publishing.
- [182] H. Zhang and J. F. Banfield, "Understanding Polymorphic Phase Transformation Behavior during Growth of Nanocrystalline Aggregates: Insights from TiO₂," *The Journal of Physical Chemistry B*, vol. 104, no. 15, pp. 3481-3487, 2000.