CHAPTER 1

INTRODUCTION

Nanotechnology literally means any technology on a nanoscale that has applications in the real world. Nanotechnology encompasses the production and application of physical, chemical, and biological systems at scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems. Nanotechnology is likely to have a profound impact on our economy and society in the early 21st century, comparable to that of semiconductor technology, information technology, or cellular and molecular biology. Science and technology research in nanotechnology promises breakthroughs in areas such as materials and manufacturing, nanoelectronics, medicine and healthcare, energy, biotechnology, information technology, and national security. It is widely felt that nanotechnology will be the next Industrial Revolution. Nanometer-scale features are mainly built up from their elemental constituents. Examples include chemical synthesis, spontaneous self-assembly of molecular clusters (molecular self-assembly) from simple reagents in solution, biological molecules (e.g., DNA) used as building blocks for production of three-dimensional nanostructures, and quantum dots (nanocrystals) of arbitrary diameter (about $10-10^5$ atoms). The definition of a nanoparticle is an aggregate of atoms bonded together with a radius between 1 and 100 nm [1].

Recently, nanostructured materials such as nanowires, nanorods, nanotubes and nanofibers have received considerable attention for a variety of applications [2];

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especially, nanofibers or non-woven textiles [3]. They have attractive properties and novel potential applications for using as solar cells, electromagnetic shielding materials, non-wetting textiles, medical prosthesis, and liquid crystal devices [4, 5]. A possible process used to produce nanofibrous inorganic materials is by electrospinning, which is now becoming increasingly popular [6] even for the industrial scale production. It is able to produce continuous polymer fibers with diameters of micro- and nano-scale through the action of an external electric field imposed in a polymer solution or melt [3]. By using the inorganic material and polymer mixtures as the starting precursors, the inorganic material–polymer electrospun fibers can be produced easily. When diameters of the electrospun fibers are lessened from micrometers to sub-micrometers or nanometers, there appear some amazing characteristics such as very large surface area to volume ratio, flexibility in surface functionality, and superior mechanical performance [5]. Subsequently, inorganic nanofibers can be produced by the calcination of inorganic material-polymer electrospun fibers obtained by electrospinning of the sol–gel solution [7].

The development of new routes for the treatment of solutions or synthesis of materials is driven by the continuing need for fast and energy-efficient techniques. For example, microwave-assisted routes are used in many areas of knowledge in new processes as well as substituting many conventional preparative methods [8]. Microwave-based methods are generally much faster, cleaner, and more economical than the conventional practices. Also, new approaches and even unexpected results have increased the interest for the use of microwave energy in many processes involving chemical reactions [8, 9]. Recently, the microwaves were introduced as an innovation in the conventional/autoclave hydrothermal process to produce a wide

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range of materials for industrial applications. It appears to be a low-energy processing route (minor environmental impact) to clean wastewaters as well as to obtain crystalline and single-phase materials at mild temperatures and pressures with morphology control [10-14]. Also, an additional advantage of the microwave-hydrothermal process is that a hazardous industrial waste may be turned into a relatively cheap and accessible source of raw material to produce a more valuable product, such as electroceramics, in comparison to the traditional sulfate and chloride salts. Finally, and especially relevant is the possibility to immobilize hazardous elements present in the effluent solution into the ceramics product. One unique process, or with few variations, can be used to treat pickling liquors from various sources, which is important to reduce capital and operating costs. In view of that, this communication aims to apply the microwave-hydrothermal technology to reduce the content of hazardous metals in spent pickling liquors to an acceptable level and also to produce high value added materials for technological applications. This is a new approach, important from both environmental and economical points of view, once it combines the pollutants removal from the aqueous phase together with the concurrent production of valuable materials [15].

For the present research, the architectural control of metal tungstates and metal molybdates with well-defined shapes is an important goal of my research because of the importance of the shape and textures of materials in determining their widely varying properties [16-23]. Thus, a number of attempts have been made to develop the preparation of metal tungstates and metal molybdates by electrospinning and microwave-hydrothermal. This method has been widely used as one of the most

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effective approaches owing to availability of flexible adjustment of the experimental parameters of the synthetic system.

1.1 Metal Tungstates and Molybdates

1.1.1 Application of Metal Tungstates and Molybdates

Metal tungstates and molybdates are two important families of inorganic material that have a high application potential in various fields, such as in photoluminescence , microwave applications, optical fibers, scintillator materials, humidity sensors, magnetic properties, and catalysis [24].

1.1.2 Structure of Metal Tungstates

a). The scheelite structures (Figure 1.1) may regarded as a cubic closepacked array of A^{2+} and $[WO_4]^{2-}$ units with the coordination numbers of 8 or 4 oxygen atoms for the A and W cations, respectively. The W atoms are tetrahedrally coordinated to oxygen. Typical oxides of scheelite structures are $CaWO_4$, $SrWO_4$, $BaWO_4$, and $PbWO_4$.

b). The wolframite structures (Figure 1.2) may be described as made up of hexagonally close-packed oxygens with certain octahedral sites filled up A and W cations in an ordered way. Typical oxides of wolframite structures are $FeWO_4$, $CoWO_4$, $NiWO_4$, $ZnWO_4$, $CdWO_4$ and $MgWO_4$.

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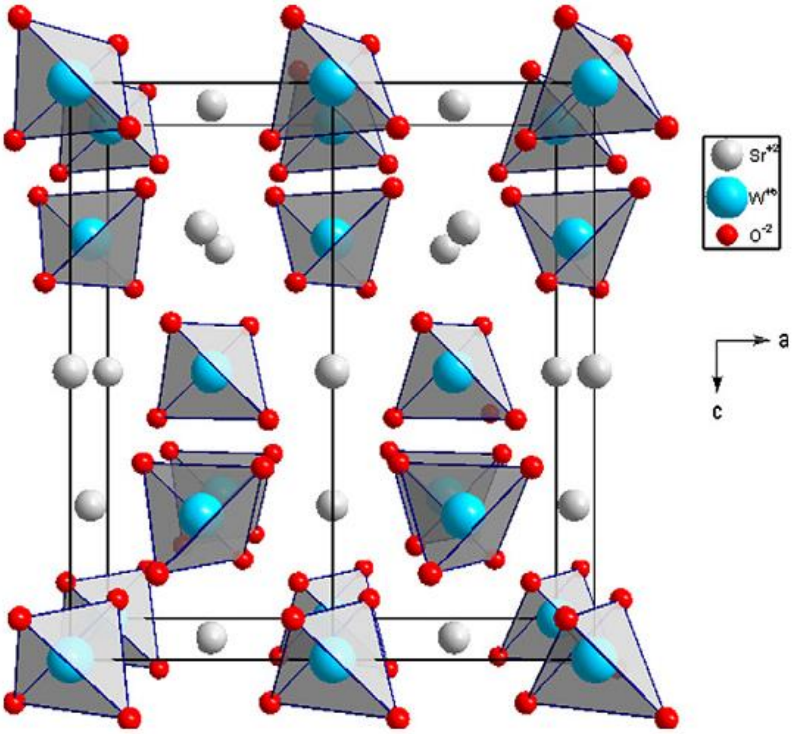

Figure 1.1 Crystal structure of $SrWO_4$ [25].

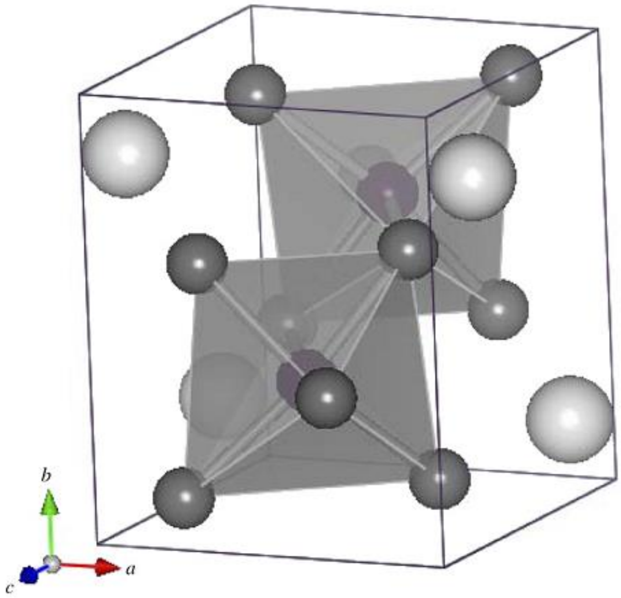

Figure 1.2 $MgWO_4$ cell unit. W ions are shown in white, O ions are shown in grey, and Mg ions are shown in black inside the coordination polyhedral formed by oxygen ions [26].

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1.1.3 Structure of Metal Molybdates

a). Scheelite structures (Figure 1.3) may regarded as a cubic closepacked array of A^{2+} and $[MoO_4]^{2-}$ units with the coordination numbers of 8 or 4 oxygen atoms for the A and W cations, respectively. The Mo atoms are tetrahedrally coordinated to oxygen. Typical oxides of scheelite structures are $CaMoO_4$, $SrMoO_4$, $BaMoO_4$, and $PbMoO_4$. (ionic radius > 0.99 Å)

b). Wolframite structures (Figure 1.4) may be described as made up of hexagonally close-packed oxygens with certain octahedral sites filled up A and W cations in an ordered way. Typical oxides of wolframite structures are $CoMoO_4$, $NiMoO_4$, $ZnMoO_4$, $CdMoO_4$ and $MgMoO_4$.

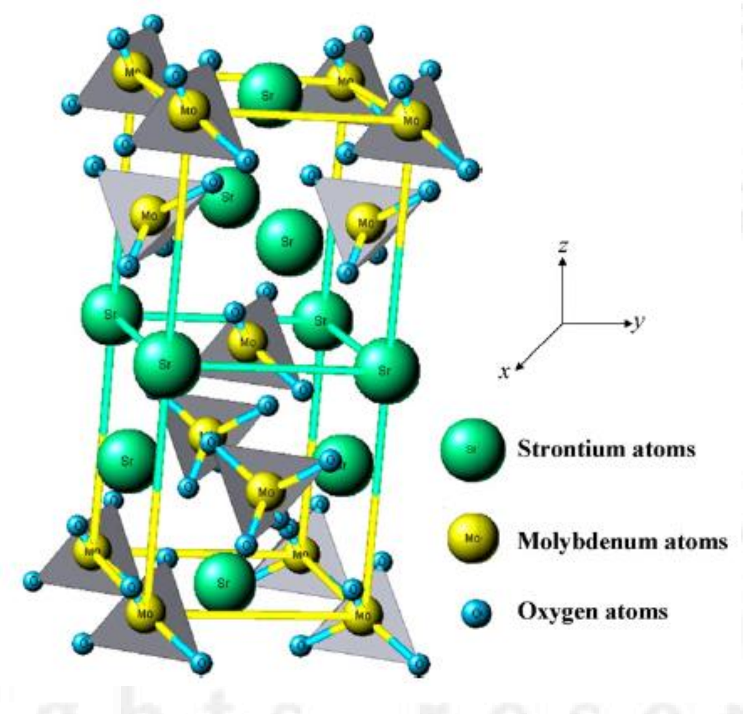

Figure 1.3 Crystal structure of $SrMoO_4$ [27].

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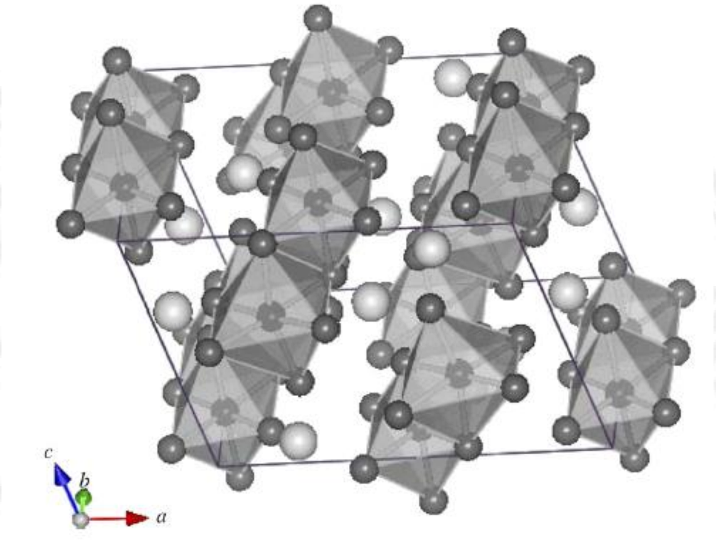

Figure 1.4 $MgMoO_4$ cell unit. Mo ions are shown in white, O ions are shown in grey, and Mg ions are shown in black inside the coordination polyhedral formed by oxygen ions [28].

1.2 Electrospinning method

Electrospinning was first observed by Rayleigh in 1897. It was studied in detail by Zeleny [29] in 1914 (on electrospraying), and patented by Formhals [30] in 1934. In particular, the work of Taylor and others on electrically driven jets has laid the groundwork for electrospinning [31].

1.2.1 Processing

a) Fundamental aspect

A schematic diagram to interpret electrospinning of polymer nanofibers is shown in Figure 1.5. There are basically three components to fulfill the process: a high voltage supplier, a capillary tube with a pipette or needle of small diameter, and a metal collecting screen. In the electrospinning process a high voltage is used to

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create an electrically charged jet of polymer solution or melt out of the pipette. Before reaching the collecting screen, the solution jet evaporates or solidifies, and is collected as an interconnected web of small fibers [32-49]. One electrode is placed into the spinning solution/melt and the other attached to the collector. In most cases, the collector is simply grounded, as indicated in Figure 1.5. The electric field is subjected to the end of the capillary tube that contains the solution fluid held by its surface tension. This induces a charge on the surface of the liquid. Mutual charge repulsion and the contraction of the surface charges to the counter electrode cause a force directly opposite to the surface tension [44]. As the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone [50]. Further increasing the electric field, a critical value is attained with which the repulsive electrostatic force overcomes the surface tension and the charged jet of the fluid is ejected from the tip of the Taylor cone. The discharged polymer solution jet undergoes an instability and elongation process, which allows the jet to become very long and thin. Meanwhile, the solvent evaporates, leaving behind a charged polymer fiber. In the case of the melt the discharged jet solidifies when it travels in the air.

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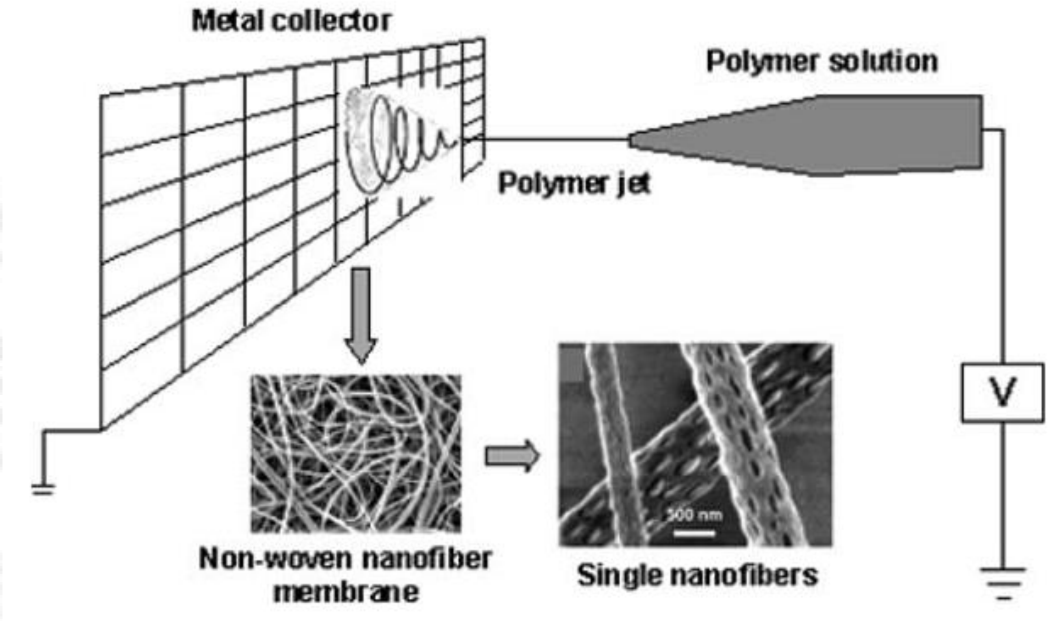

Figure 1.5 Schematic diagram to show polymer nanofibers by electrospinning.

b) Parameter investigation

Many parameters can influence the transformation of polymer solutions into nanofibers through electrospinning. These parameters include (a) the solution properties such as viscosity, elasticity, conductivity, and surface tension, (b) governing variables such as hydrostatic pressure in the capillary tube, electric potential at the capillary tip, and the gap (distance between the tip and the collecting screen), and (c) ambient parameters such as solution temperature, humidity, and air velocity in the electrospinning chamber [38].

Another problem encountered in electrospinning is that defects such as beads Figure 1.7 [51], and pores Figure 1.6 may occur in polymer nanofibers. It has been found that the polymer concentration also affects the formation of the beads. Fong [48] recognized that higher polymer concentration resulted in fewer beads. In their

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experiments with PEO polymer, the polymer concentrations of 1 – 4.5 wt.% were used. The resulting fiber membranes were visualized under SEM, and different fiber morphologies were captured, as shown in Figure 1.8, in which the lowest viscosity, 13 centipoise, corresponded to 1 wt.% PEO concentration, whereas the highest viscosity, 1250 centipoise, corresponded to 4 wt.% conentration. It should be realized that with the 4 wt.% PEO concentration the beads were not reported to completely disappear. Instead, the bead diameters, if any, at higher concentrations were even larger. The shape of the beads changed from spherical to spindle-like when the polymer concentration varied from low to high levels.

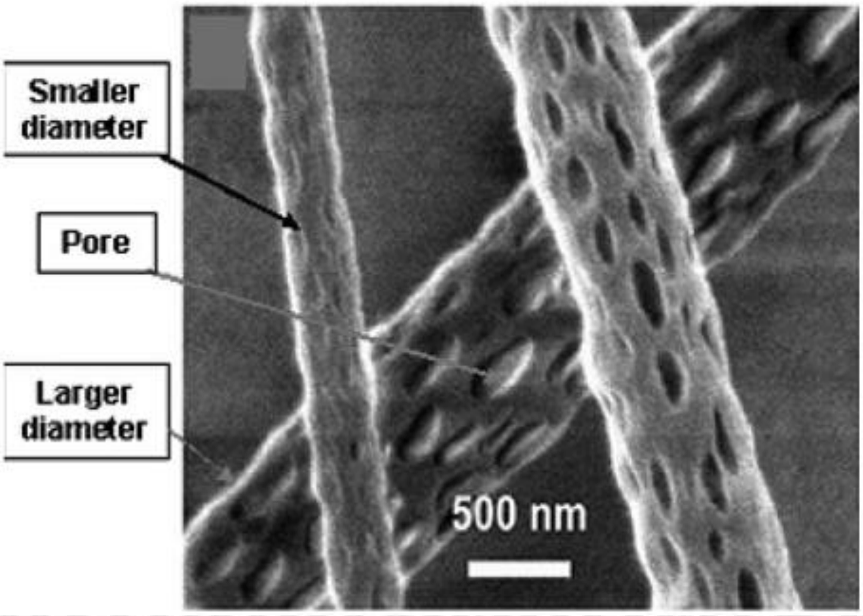

Figure 1.6 PLLA nanofibers with different diameters and pores [52].

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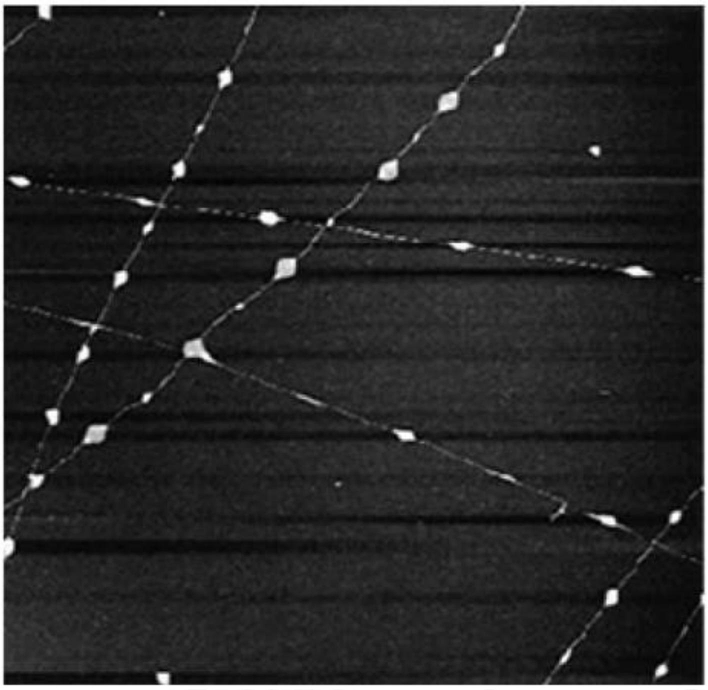

Figure 1.7 AFM image of electrospun PEO nanofibers with beads [51].

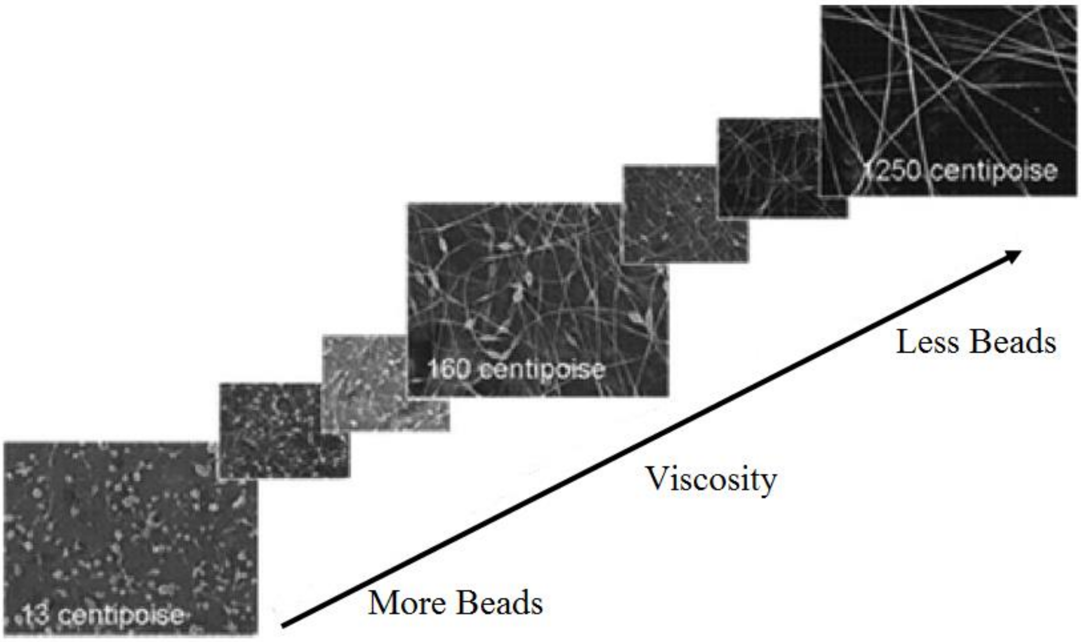

Figure 1.8 SEM photographs of electrospun nanofibers from different polymer concentration solutions [48]

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As the charges carried by the jet increased, higher elongation forces were imposed to the jet under the electrical field, resulting in smaller bead and thinner fiber diameters. This, however, does not imply that a higher applied electrical field could result in fewer beads and smoother nanofibers. In fact, Deitzel et al. investigated the influence of electrical charge, which was applied for electrospinning, on the morphology of PEO nanofibers [32]. They reported that with the increase of the electrical potential the resulting nanofibers became rougher. Their results are shown in Figure 1.9

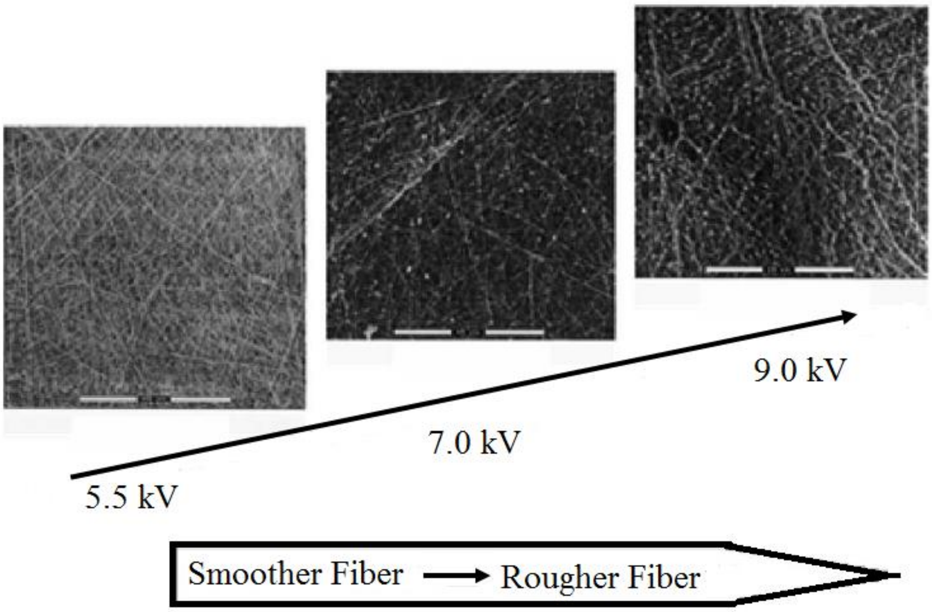

Figure 1.9 SEM photographs of PEO nanofibers electrospun under different electrical potentials [32].

1.2.2 Applications

Reviewing the number of patents, one can see that approximately two-thirds of all electrospinning applications are in the medical field. Of the remaining patents, one-half deals with filtration applications, and all other applications share the remaining

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half. The potential applications of nanofibers have been reviewed, as shown schematically in Figure 1.10. A very broad range of applications-including life sciences, medical, and filtration applications as well as sensors, protective clothing, and masks is covered.

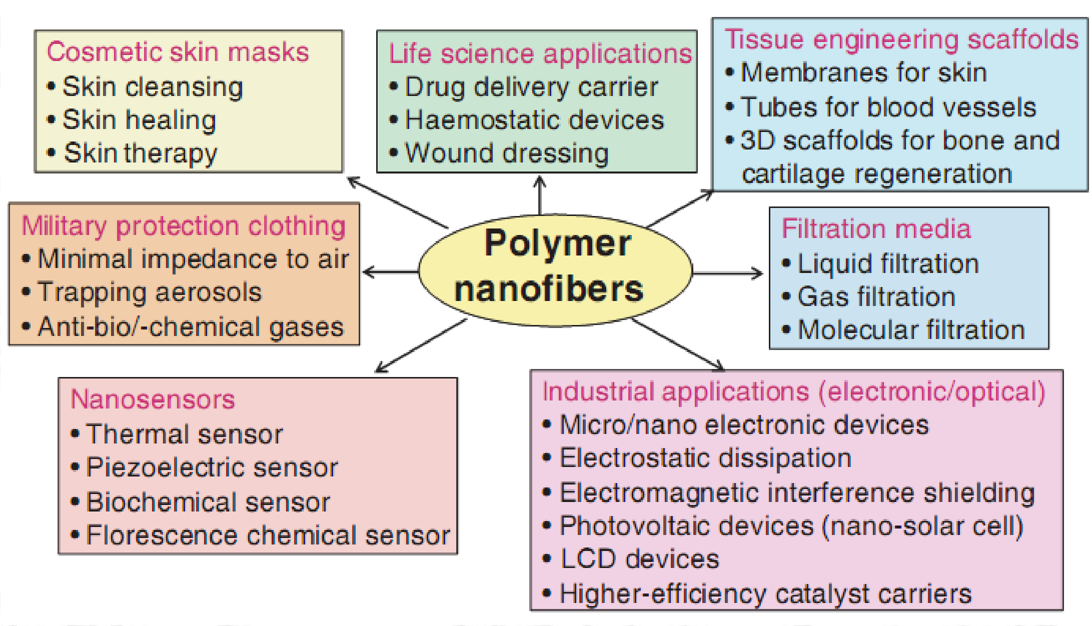

Figure 1.10 Potential applications of electrospun polymer nanofibers.

1.3 Microwave method

Microwave is electromagnetic radiation with frequency range of 0.3-300 GHz. Microwave heating leads to the direct interaction between microwave radiation and materials. Firstly, microwave radiation couples with the material and then it is absorbed by the material. So, electromagnetic energy is converted to thermal energy [53]. Microwave irradiation as a heating method has been used for a number of applications in chemistry. The application of microwave heating in synthetic chemistry is a fast-growing area of research. Microwave heating leads to the direct interaction between microwaves and materials and this fact enables a uniform and fast

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heating of a sample. This difference can result in many potential advantages for microwaves in processing of materials. Another fundamental difference between microwave heating and conventional heating is that heating under microwave irradiation occurs in an in–out fashion, i.e. from the solution to the flask, while with conventional heating energy is transferred out–in, i.e. from the flask to the solution. Therefore, microwave-assisted synthesis is a fast, low cost and simple method [54-55]. It has been developed and is widely used in many areas such as the preparation of inorganic complexes and oxide, organic reactions, plasma chemistry, analytical chemistry and catalysts. The applications of microwave irradiation in the preparation of nanocrystalline materials have been reported in recent years. Microwave irradiation has shown very rapid growth in its application to materials science due to its unique reaction effect such as rapid volumetric heating and the consequent dramatic increase in the reaction rate. Comparing to the conventional methods, microwave synthesis has the advantages of short reaction time. The products have small particle size, narrow particle size distribution and high purity [56-61]

1.4 Hydrothermal/Solvothermal method [22]

The hydrothermal/solvothermal method is one of the most promising solution techniques for advanced materials processing. The reaction can be carried out in water or in any other solvent. When water is used as a solvent, the process is called “hydrothermal process” and when non-aqueous / organic solvents such as methanol, ethanol, polyol, etc. are used, the process is termed “solvothermal process”. In the usual hydrothermal process, the starting chemicals are dissolved in water. This solution is placed in a reactor (Figure 1.11) and the chemical reaction is carried out in

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closed systems under autogenous pressure and elevated temperature, which allow for greater solubility of solids for the reaction process, and the desired compounds can be synthesized at lower temperatures compared to the solid-state reaction method. This method has several advantages over the other conventional processes like saving, simplicity, cost effectiveness, better nucleation control, pollution free (since the reaction is carried out in a closed system), higher dispersion, higher rate of reaction, better shape control, and lower temperature of operation in the presence of an appropriate solvent, etc. The hydrothermal technique has a lot of other advantages like it accelerates interactions between solid and fluid species, phase pure and homogeneous materials can be achieved, reaction kinetics can be enhanced, the hydrothermal fluids offer higher diffusivity, lower viscosity, facilitate mass transport and higher dissolving power. Most important is that the chemical environment can be suitably tailored [62].

Figure 1.11 General purpose autoclave popularly used for hydrothermal synthesis [63].

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The hydrothermal processing of materials is a part of solution processing and it can be described as super-heated aqueous solution processing. Figure 1.12 shows the pressure temperature map of various materials processing techniques [64]. When the production processing goes out of ambient temperature to higher or lower temperature and pressure condition to higher or lower pressure directions, particularly to vacuum, environmental loads would increase. In this regard, we cannot depend only on the high-technology industry for materials processing. On the other hand, solution processing is located in the p–T range characteristics of ambient conditions where all lives are living on the earth. Thus, solution processing should be the most environmentally friendly and should be used more as a low-energy process for producing even various artificial materials [65]. According to this, the hydrothermal processing of advanced materials can be considered as environmentally benign.

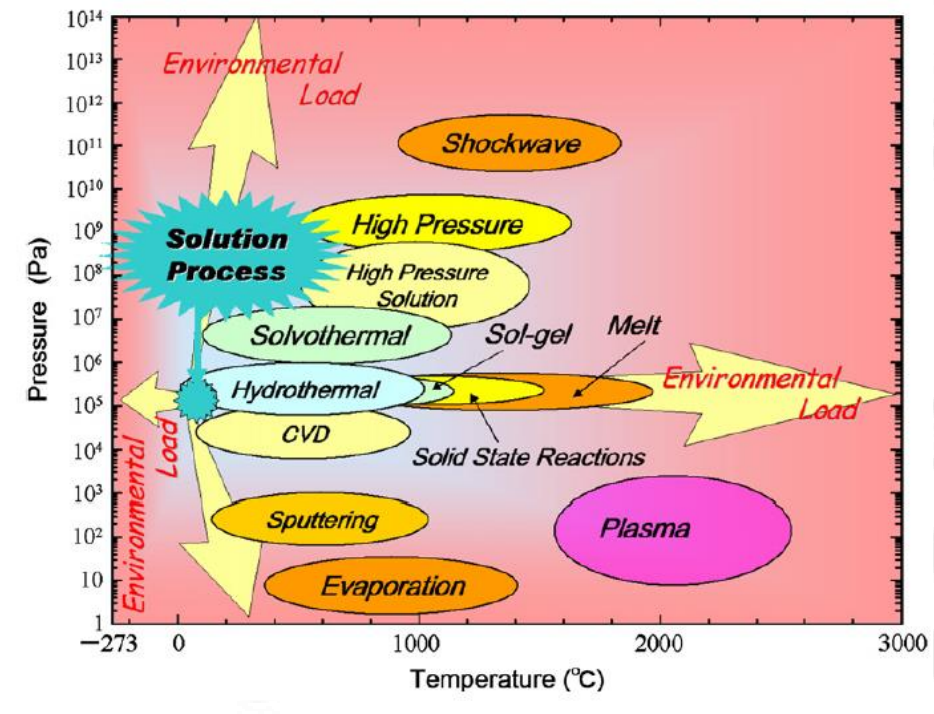

Figure 1.12 Pressure temperature map of materials processing techniques [64].

1.5 Microwave- Hydrothermal method

As a novel technology microwave processing of materials can provide the material processor with a powerful and significantly different tool to process materials that may not be amenable to conventional means of processing. In microwave heating, the continuous electromagnetic waves are produced in the magnetron and transmitted through a hollow metallic tube into a resonant cavity where the materials are to be processed [66-69]. Materials are heated due to their molecular frictions caused by alternating polarization of molecules, which involves two main processes, namely dipolar polarization and ionic conduction. Since the electromagnetic radiation can produce an oscillating field, which results in alignments of the dipoles or ions of the samples along the direction of electric field. Due to the time scales of the orientation and disorientation phenomena relative to the frequency of the microwave irradiation, different amounts of heat are produced through the molecular friction and dielectric loss. As the rotation frequencies of many polar molecules in the liquid begin to lag behind the frequency of electric field oscillations, a resistive heating begins to be produced within the medium. This is named as dielectric loss, which is the portion of the energy of an alternating electrical field in a dielectric medium that is converted into heat and lost in the sample. In the case of ionic conduction the dissolved charged particles oscillate back and forth under the influence of the microwave irradiation, collide with neighboring molecules, and thus generate heat. It is important to note that the ionic conduction mechanism represents a much stronger effect than the dipolar polarization with respect to the heat-generating capacity, and this has of course great consequences for the synthesis of nanoparticles in ionic liquids. However, due to the complexity of microwave interactions with materials, in order to heat the sample

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efficiently in microwave oven, experimental parameters (e.g., irradiation power, reaction temperature and pressure inside the vessel) must be controlled precisely. Over the past years hydrothermal synthesis as a well-established and promising approach, has been used to synthesize oxide nanomaterials, starting from binary oxides (e.g., ZnO, CuO, MgO, TiO2, SnO_2) to ternary oxides (e.g., $BaTiO_3$, $PbTiO_3$, $BiFeO_3$, $KNbO_3$), and then to more complex compounds (e.g., $Ba_{1-x}Sr_xTiO_3$, $La_{0.5}Ca_{0.5}MnO_3$, $La_{0.325}Pr_{0.300}Ca_{0.375}MnO_3$) [70]. The advantage of this approach is its low synthesized temperature compared with the traditional solid-state and vapor-phase reactions, and also the hydrothermal process gives rise to the crystalline products without any further post-annealing treatment (e.g., calcination required after sol‑gel process) [71]. However, the conventional heating in hydrothermal process relies on thermal conduction of black-body radiation to drive chemical reactions, whereby the reaction vessel serves as an intermediary for energy transfer from heating source to the solvent, and finally to the reactant molecules. So, this heating manner inevitably suffers from several disadvantages especially at low temperatures, such as the long initial heating period that may result in inhomogeneous temperature profiles within the autoclave and slow reaction kinetics, leading to poor nucleation and broad size distributions of the products. To address the problem of heating inhomogeneity, and to enhance the crystallization kinetics of hydrothermal process, M-H process was developed and coined by Komarneni et al. [72], which has been received much attention due to its many distinct advantages over the conventional hydrothermal process. For example, in the Microwave - Hydrothermal method process, the microwave radiation couples with the reaction mixture, and the electromagnetic energy is converted into thermal energy, which is absorbed by the reaction mixture.

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Therefore, the heat generated inside the reaction mixture makes it rapidly and homogenously to the desired temperature due to extremely rapid kinetics of crystallization (one-to-two orders of magnitude). Now the Microwave - Hydrothermal method process become as a promising approach towards the synthesis of low-dimensional nanostructured materials. In addition, it also allows one to synthesize nanomaterials with novel or metastable phases due to the fast crystallization kinetics [73].

1.6 Research objectives

1. To build and develop the homemade electrospinning and microwave-hydrothermal equipments.
2. To synthesize $SrWO_4$, $MgWO_4$, and $MgMoO_4$ with nanofibrous structures by electrospinning technique.
3. To synthesize $SrMoO_4$ with flower-like shape by microwave-hydrothermal technique.
4. To characterize the synthesized products using their characterization tools.

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