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Fabrication and Characterization of Polyvinylpyrrolidone/Cu^{2+} Nanofibers

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Abstract of the Thesis

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Polymer/transition metal salt composite nanofibers have gained considerable attention in recent years. Doping of transition metal salt into the polymer matrix allows the fabrication of nanofibers with special functions. This goal of this study is to develop PVP/Cu^{2+} composite nanofibers for potential optical application.

In this study, polyvinylpyrrolidone(PVP)/Cu^{2+} nanofibers with diameter of 200-900 nm were fabricated by electrospinning. Coper(II) nitrate trihydrate was added to PVP electrospinning solution. The electrospun nanofibers were characterized by scanning electron microscope(SEM), energy dispersive microscopy(EDS), and ultraviolet–visible spectroscopy(UV-vis). The results indicate that Cu^{2+} was successfully doped into PVP system and the electrospun PVP/ Cu^{2+} nanofibers show a board band at 780nm on the absorption spectrum. It also suggest that the fibers became fine and had higher absorption intensity with PVP/Cu(NO$_3$)$_2$ weight ratio decreasing.

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CHAPTER 1: INTRODUCTION

Nanomaterials have been studied with great interest due to their many advantages over bulk materials. Among different kinds of nanoscale materials, nanofibers have been widely applied in many scientific fields due to their easy processability and special porous structures (Lee and Im 2010). Nanofibers are generally characterized as fine fiber with their size down to tens to hundreds of nanometers (Zhou and Gong 2008). Compared with conventional bulk materials, nanofibers are light, small in size, and have high ratio of surface to volume, which make them a suitable candidate for tissue engineering (Li, Laurencin et al. 2002), sensor technology (Ding, Wang et al. 2009), and batteries applications (Ramakrishna, Fujihara et al. 2006), etc.

Polymers are flexible, easy processed, and light-weighted materials, while metal are hard materials possessing chemical, optical, and magnetic properties, etc. Fabrication of polymer/metal salt composite nanofibers gained increased interest, because they could take advantage of both of the organic and inorganic materials properties(Hagrman, Hagrman et al. 1999). Doping of transition metal salt into the polymer matrix allows the fabrication of nanofibers with special functions. They have many potential applications, such as emissive materials, optical limiter, catalysis, ionic conductors, and sensors (Wei 2012).

1.1 Functional Composite Nanofibers

Functional materials are commonly referred to those materials having their unique

functions due to specific structures and properties. The incorporating of different components into functional materials in the form of fiber can promote their properties to a higher level. Functional composite nanofibers have shown enormous potential in medical area, energy storage, etc (Ashammakhi, Wimpenny et al. 2009). In general, they can be classified into polymer/polymer composite nanofibers and polymer/inorganic composite nanofibers.

1.1.1   Polymer/polymer composite nanofibers

Application

Polymer/polymer composite nanofibers are generally composed of two or multiple polymers. They have been applied in many scientific fields especially in tissue engineering and medicine research. For example, in tissue engineering the using of nanofibers as scaffolds can resemble structure of the native extracellular matrix (ECM) physically and chemically to allow tissue to grow on it over a period of time (Zhu, Cui et al. 2008). Several polymer/polymer composite nanofiber with this function have been developed. For example, electrospun Polypyrrole(PPy)/PLGA nanofibers were developed as a scaffold in neural tissue engineering and cell culture show it is preferable for cell growth than PLGA nanofibers alone (Lee, Bashur et al. 2009). These study suggest polymer/polymer nanofibers may function better compared to nanofibers made from single polymer.

Synthesis Method

Polymer/polymer composite nanofibers can be fabricated by direct electrospinning or co-electrospinning. Polymer using as functional component can be added into co-electrospinning

system, allowing the fabrication of functional nanofibers in core-shell structure.

1.1.2   Polymer/inorganic composite nanofibers

Application

Polymer/inorganic salt composite nanofibers have gained much interest due to their special applications including photographic and optical materials, catalysis, ionic conductors, and sensors. Rare earth salts and transition metal salts are used as dopant easily accepted by polymer matrix. Polymer/nanoparticle composite nanofibers, consisting of nanoscale inorganic component and a polymer matrix, encompass the advantages of both organic and inorganic materials. The synthetic materials of this kind are usually flexible with high strength, lightweight with heat stability, possessing chemical, optical, electrical properties (Dzenis 2004).

Many works have been done to develop polymer/inorganic nanofibers to expand the application of polymers to a wider range. Integrating nanoparticles with polymer system to produce composite fibers with special functions such as Au doped PEI/PVA nanofibers (Fang, Ma et al. 2011) and Pd PANI composite nanofibers (Gallon, Kojima et al. 2007) for catalytic application and . Another example is developing Fe-montmorillonite PA6 composite nanofibers and studying their properties with spectroscopic tools (Cai, Huang et al. 2008). The result indicates metal component was successfully dispersed into polymer fibers system with improved thermal, mechanical and crystallinity. Discussion above proved that polymer/inorganic nanofibers possessing different properties could be applied to different kinds of scientific fields.

Synthesis Method

Many techniques were explored in synthesis of polymer/inorganic nanofibers, including sol-gel method, electrospinning, etc. Sol-gel method, being an effective routine of preparing precursor, is always used along with electrospinning technique. Many polymer/inorganic materials were prepared this way. For example, functional component zinc oxide was dispersed onto electrospun PAN nanofibers surface by sol-gel method (Shao, Wei et al. 2008). The results showed that ZnO was incorporated evenly on the nanofibers and the synthetic nanofibers are functionalized due to a modified crystalline structure. Typically electrospinning is used alone in the synthesis of polymer/metal salt nanofibers. Inorganic salts are added to the polymer electrospinning solutions and ultrasonicated. Then mixed solution will be used in electrospinning to form polymer/inorganic salt hybrid nanofibers or be reduced to nanoparticles. For example, $AgNO_3$ was doped into PAN solution, and electrospun to form hybrid nanofibers, which can be later processed for forming nanoparticle (Lala, Ramaseshan et al. 2007).

1.2 Polymer/Metal Composite Nanofibers for Optical Application

Some unique properties can be achieved by polymer nanofibers doping with metal salts (Xu, Inai et al. 2004). The interaction of transition metal salt or rare earth salt with the polymer ligand could alter the microenvironment of metal ions, which makes them possible to be used in optical application as optoelectronics, emissive materials, and optical limiter.

It has been reported that metal containing polymers have applications in the field of emissive materials and optical limiter. Transition metals or lanthanides have been used as emitter center in the synthesis of emissive polymers. Ru^{2+} and Ir^{3+} were doped into polymer system to form metal

polymer complex, which have a potential application to be used as light emitting diodes and light emitting electrochemical cells (Holder, Langeveld et al. 2005).

Optical filter is another potential application that polymer/metal composite nanofibers could develop to. Optical limiters are instruments used to filter wavelength in the optical path, which can make wanted wavelengths to pass, and scatter or absorb the unwanted ones. They are characterized by their frequency, which describes how much the intensity and phase of different frequency component of an incoming light have been changed after passing a filter (Madsen and Zhao 1999). Silver nanoparticles doped polystyrene was studied for its optical properties by UV-vis spectroscopy, which suggests its potential to be developed as a color limiter(Carotenuto, Palomba et al. 2011).

Luminescent rare earth ion and complex of Eu were widely studied by incorporating them into polymer to form polymer /rare earth composite nanofibers. The study of $Eu(BA)_3(TPPO)_2$/PVP composited nanofibers shows its strong photoluminescent ability (Zhang, Song et al. 2007). In another study, the optical properties of PVP/Eu^{3+} electronspun nanofiber were compared to PVP/Eu^{3+} film (Tang, Shao et al. 2010). It has been reported that transition metal ions like Cu^{2+} and Co^{2+} were successfully doped into polymer film. The optical study indicates their light absorption ability due to the d-d transition and their green emission appeared on emission spectra (Sivaiah, Rudramadevi et al. 2010). The examples above show that nanofibers have an improved optical property due to the applied electric field in electrospinning and high surfave to volume ratio specification. This may lead to the further development of polymer/metal nanofibers by electrospinning for optical applications.

1.3 PVP as Matrix

1.3.1 Structure
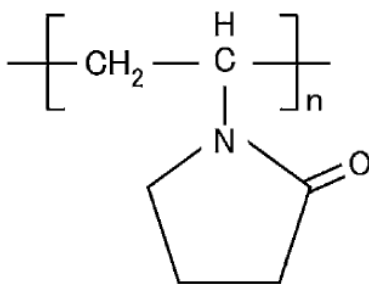
Figure 1Structure of Polyvinylpyrrolidone(PVP) (Koga, Yakushiji et al. 2010)

Polyvinylpyrrolidone(PVP) is made from monomer N-vinylpyrrolidone having a structure as shown in Fig 1. PVP is an amorphous polymer with active C=O groups, which made it suitable to interact with metal ion for fabricating functional composite materials (Lu, Zhao et al. 2005). When C=O groups of PVP coordinating with transition metal ions, the microenvironment of ions could be affected, which may lead to the change of energy transfer probabilities during electron interacting with atoms(Tang, Shao et al. 2007).

1.3.2 Properties

PVP have many properties, such as linear ionic, adhesive, water solubility, and compatible with various materials. Some of its properties and corresponding commercial applications are listed in Table 1.

Table 1 Properties and applications of PVP (PVP Brochure, Brenntag Specialties,Inc)

Property	Application
Able to attach to glass, metal, plastic	Adhesives
Able to accept inorganic materials	Ceramics
Backbone grafting monomer	Fibers
Porosity and filtration ability	Membrane
Able to form complex and gels in water	Environmental Protection
Particle size regulation and viscosity modifying in polymerization	Polymerization

The choosing of PVP as matrix in this experiment is because they were found to be easily doping with transition metals. Typically PVP is regarded as an inert polymer, however it was found having the ability to interact with different kinds of smaller molecules to form complex (Wu, Wu et al. 2001). Thus PVP materials seem to be a suitable matrix attribute to this property. Metal ion such as Tb^{2+}, Eu^{3+} has been explored as dopant embedded into PVP polymer matrix (Sivaiah, Rudremadevi et al. 2010). By doing this it is possible to convert PVP to bright luminescent material which is of importance for optical application.

Other reasons of choosing PVP over other conjugated polymers owing to its nontoxic nature and being easily processed in solutions. Also its good sustainability and low cost makes

PVP a good matrix in various experiments.

1.4 Doping with Copper Ion

As mentioned above, the using of rare earth metal ion like Tb^{2+}, $Eu^{3+}$and transition metal ion like Ru^{2+} as luminescent component to dope into polymer system have attracted many researchers. However, these materials are relatively at high cost and low sustainability. So it's necessary to look for other substitute that would be suitable to form a polymer/metal composite nanofibers for optical applications. Transition metal salts like copper salt and cobalt salt are comparable inexpensive and might be a good candidate in employing it as a dopant with PVP to improve optical properties of polymer.

There are a few investigations on fabricating polymer/Cu^{2+} film. For example, Polyvinylalcohol (PVA) film showed a property improvement after doping with copper salt, which indicated their application as a optical device (El-Khodary 2010). However, the study on preparing Cu^{2+} doped PVP materials in the form of fibers seems new. So it's of challenge and importance to explore the application potential of PVP/Cu^{2+} nanofibers due to its specific structure over conventional PVP/Cu^{2+} materials.
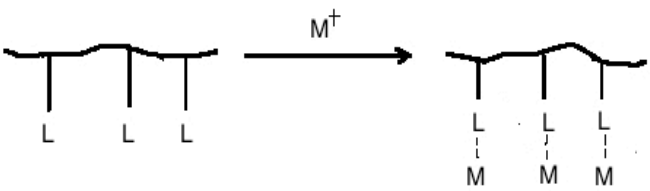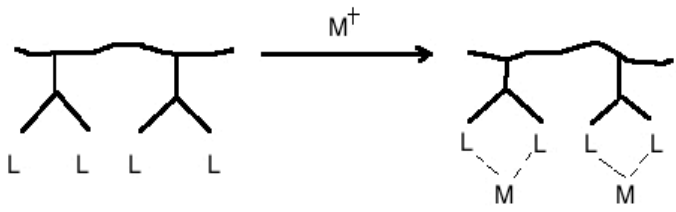
1.5 Metal Ligand Interaction
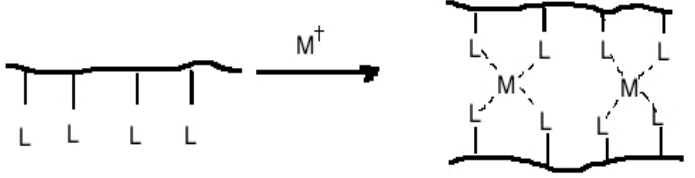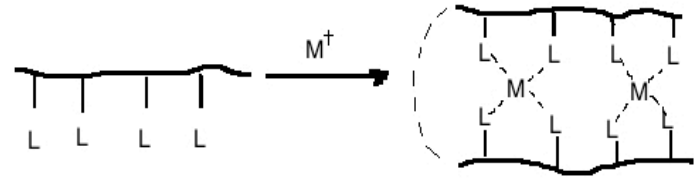
In this experiment, PVP and copper ions coordinated in the process of preparing of their electrospinning solutions. It's essential to understand the interaction between metal and ligand of polymer. In metal polymer coordination, functional group of polymer can be regarded as a ligand bonding to metal centers. The integration of metal or metal salt allow the modification of polymer in chemical, optical, and redox properties (Manners 2006). Thus the polymer metal

complex is emerging as a new kind of materials with specific structures and functions (Diaz, Valenciano et al. 2004).

The basis of polymer metal complex is to utilize metal ligand interactions with polymers. Various coordination structures can be obtained by the coordination of polymer ligand with metal ion or metal complex. According to the structure type, polymer/transition metal complex can be classified to monodentate, polydentate, intra-polymer, and inter-polymer complexes as listed in Table 2, where "L" represents ligand, and M^+ represents metal ion.

Table 2 Differenct structures of polymer metal complex (Braun 2010)

Complex type	Structure	Formation condition
Monodentate		One coordination site of metal vacant
Polydentate		Multidentete ligands present in polymer backbone

Intra-polymer		Metal ion has multiple bonding sites
Inter-polymer		

Cu^{2+} is assigned to d9 transition metal ion, which has 9 electrons in d-orbitals and 6 coordination sites. With the understanding of crystal field theory, in order to fulfill the stable state of a polymer/transition metal complex, polymer ligands will act as negative charge points to accommodate the included Cu^{2+}, on the other side. As shown in Fig 2, Cu^{2+} commonly present as an octahedral geometry where the metal center is surrounded by six ligands at the coordination sites. PVP is attracted by positive charged metal ion center derived by electrostatic force therefore no electron exchanging involved. As the ligand approaching the electrons of d orbitals, it would be repulsed, which would explain the energy increasing in d-orbitals shown in the following content.
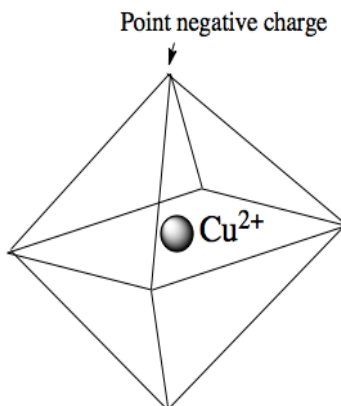
Figure 2 Octahedral model of PVP/Cu^{2+} complex

1.6 d-orbitals of Copper

When it comes to transition metals, its d-orbitals attract great attention because it gives metal versatility. The different filling configurations of d-orbitals give rise to optical, magnetic and catalysis properties. The region of an atom out of its nuclei refers to the electron cloud/configuration, and it has been defined into two structures as electron shells/energy levels and electron orbitals. Energy levels, characterized as high energy level and low energy level, have d-orbitals placed in different energy levels filled with electrons. In preceding paragraphs, the interaction of polymer ligands with d-orbital electrons of copper will be introduced, as Cu^{2+} is one of the most indispensable components for this synthetic functional nanofibers. All five d-orbitals are shown as below, they are d_z^2, dxy, dxz, dyz , and $d_x{}^2{}_{-y}{}^2$, respectively.
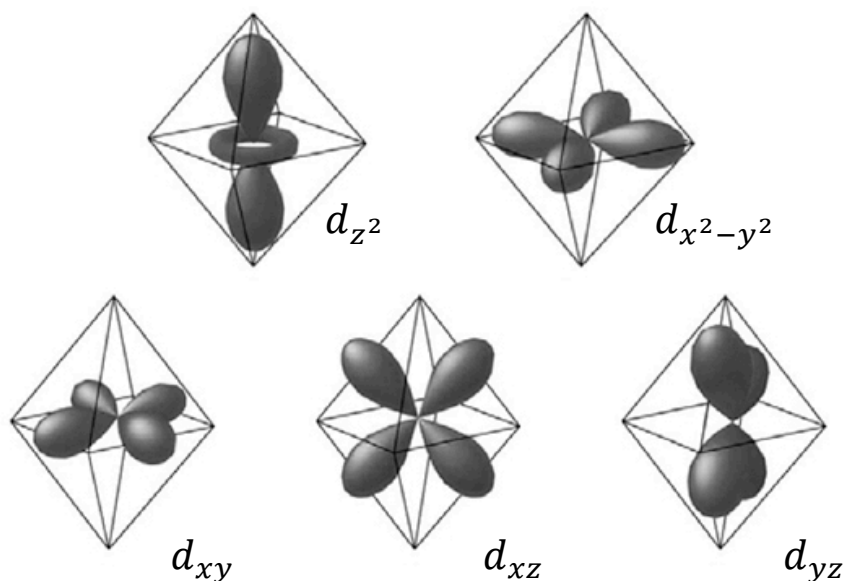
(a)
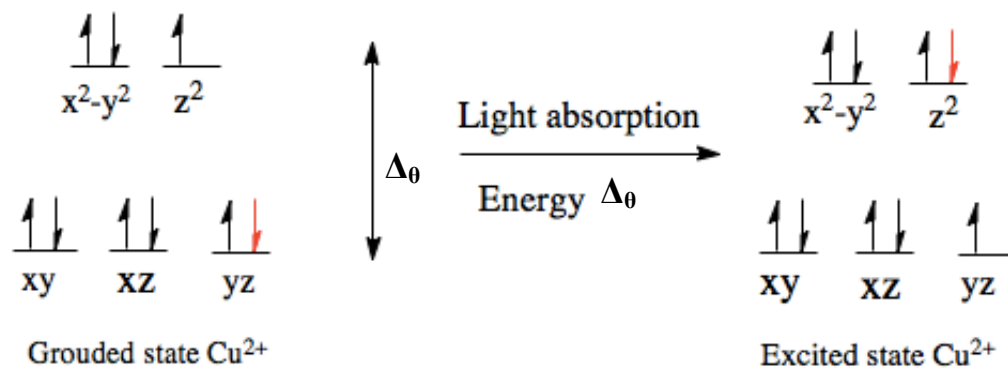
(b)

Figure 3 (a) d orbitals of Cu2+; (b) Schematic drawing of excitation of Cu^{2+} absorbing light

Hypothetically, Cu^{2+} complex is spherical structure that all the five d-orbitals are in the same energy level with average energy. In fact, on the other side, Cu^{2+} complex has an octahedral geometry that the energy level of d-orbitals will split as the same charges become in vicinity towards the positive nuclei. The configuration of a Cu^{2+}/ligands complex is shown in Fig

2, on a sub-atomic level. Atomically in the d-orbitals, the repulsive force field increases the potential energy of the orbital electrons.

As the model illustrated above, there are six negative points reorganized into an octahedral formation centered in the encased Cu^{2+}, yielding a surrounding electric field that imposes on the five d orbitals. Combining this model with five different orbitals as shown in Fig 3 (a), it is obvious that the x^2-y^2 and z^2 orbital are more closely interacting with the octahedral points than the rest orbitals, thus as illustrated in Fig 3 (b), the x^2-y and z^2 orbital are placed in a higher energy level and xy, xz and yz orbitals are put in a lower energy level. There is an energy gap between higher and lower level, namely Δ_θ. In summary, the ground state Cu^{2+} have a configuration of 3 spans on the higher level, and 6 spans in the lower level. According to the crystal field theory, the different energies of each d orbital due to the geometry can be predicted. Nine electrons paired to occupy 4 d-orbitals and one unpaired electron occupies z^2 orbital with one vacancy left.

And it is proved that the electron in yz orbital has a higher probability to jump up to the z^2 orbital by absorbing a small energy, especially red light photons, in more popular words a d-d transition occurs. This transition leads to a vacancy gap in the light spectrum through or reflecting the complex, rendering a blue color. These phenomena can be seen in various transit metal ion complex, such as blue colored hydrated copper ion (bivalent), greenish hydrate ferrous iron ion, hydrated ferric iron ion in brownish yellow etc. Those common examples share the same mechanism just by changing the source of negative charges and coordinating configurations.

1.7 Electrospinning

Spinning method of producing fibers including wet, dry, melt and gel spinning, are able to fabricate polymer fibers down to the micrometer size (Sawicka and Gouma 2006).Compared with these conventional methods, electrospinning is a superior technique of fabricating fine down to the range of 10 nm to 1 μm (Kirecci, Özkoç et al. 2012).

The big advantage of electrospinning technique is relatively cheap compared with other methods to fabricate uniform and continuous nanofibers. Materials used in electrospinnging are from different kinds of polymers. The utilizing of elctrospinning allow to produce nanofibers effectively at low coat and fabricate two dimensional and three dimensional nanofiber with applications in nanotechnology (Dzenis 2004).

1.7.1 Electrospinning Setup

Electrospinning can be characterized as a process of fabricating nonwoven, fibrous nanomaterials. As shown in Fig 4, high voltages power supply, a metering pump, a syringe with needle, and a grounded collector consist of the most common electrospinning setup vertical or horizontal.
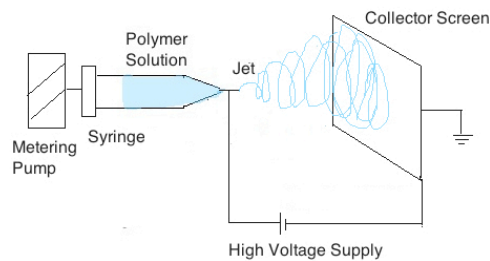
(a)
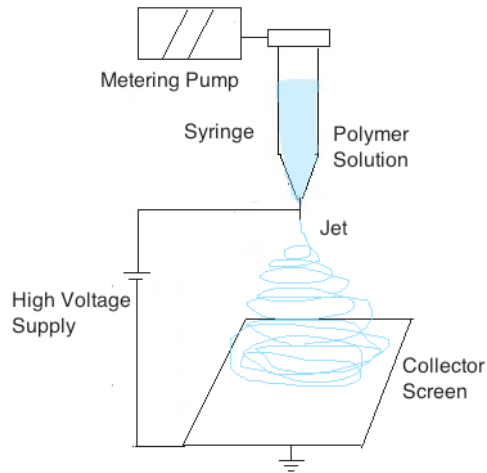
(b)

Figure 4 Electrospinning setup (a) horizontal; (b) vertical

1.7.2 Electrospinning Process

Pumping liquid droplet gets charged when sufficient power applied, causing electrostatic repulsion counteracting the surface tension, and stretching the droplet. Once voltage reaches a specific value, a liquid stream comes out of the droplet surface forming cone shape. This critical moment of eruption is defined as the Taylor cone. However, if the molecular cohesion of the liquid is high enough to overcome electrostatic repulsion, stream could not be ejected. When jet drying from the tip of needle to the substrate, current flow switching its previous mode to a mode called convective due to the movement of charge.

After current flow change, electrostatic repulsion, starting from fiber little bending area leading to whipping process which eventually make the jet elongate. It suggests that bending instability may drive the fiber to elongate towards fining. As a result, the uniform fibers with nanoscale dimension can be derived.

1.7.3 Electrospinning Mechanism

As mentioned above electrospinning have a very straightforward set up, however the mechanism of electrospinning is not that simple (Li and Xia 2004). Experiment was conducted to reveal the eletrospinning mechanism, and result suggest that bending instability caused the jet become thin (Huang, Zhang et al. 2004). As shown in Fig 5, when jet just comes out of the tip of the needle it flies almost straight but then it gets unstable during flying in the air to the collector. This instability makes the jet flying in loops, and as jet gets closer to the collector loops get larger. The loops of jet finally reach the collector and deposit on it.
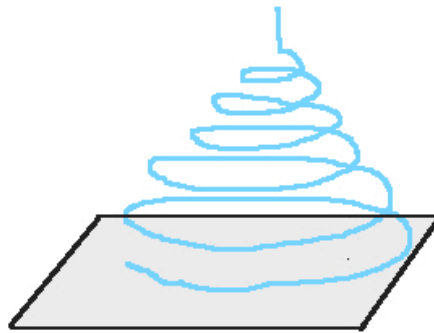
Figure 5 Schematic drawing of jet loops caused by bending instability

Electrostatic force in a bending jet, which caused bending instability, can be calculated by an equation below (Yarin, Koombhongse et al. 2001).

Equation 1 Electrostatic in a bending jet (Yarin, Koombhongse et al. 2001)

$$\text{F} = -\sigma_s^2 \ln\left(\frac{L}{a}\right)|\text{k}|\text{d}\xi$$

Where σ_s refers to surface charge, L is bending length, a is the bending radius, k is curvature of fiber and ξ is a coordinate factor. This equation gives a better understanding of

electrospinning mechanism by estimating the force which drive the bending instability.

1.8 Effect of Electrospinning Parameters

It is hard to point out which single factor is dominant in determining the morphology and diameter of electrospun fibers, because lots of parameters work on it. They can generally be divided into solution parameters and processing parameters.

1.8.1 Solution Parameters

Concentration

As shown in Fig 6, when the concentration of solution is very low, particles form at micro/nanoscale. At low concentration, which viscosity of solution is low and surface tension is high, spraying occurs rather than electrospinning (Deitzel, Kleinmeyer et al. 2001). Both beads and fibers are achieved at the same time when concentration goes higher slightly. As concentration reaching at suitable range, uniform and smooth nanofiber will be obtained. However, if the concentration is too high, ribbon shaped fibers with sized larger than nanoscale can been seen (Yang, Li et al. 2004).

Concentration Low ➔ High
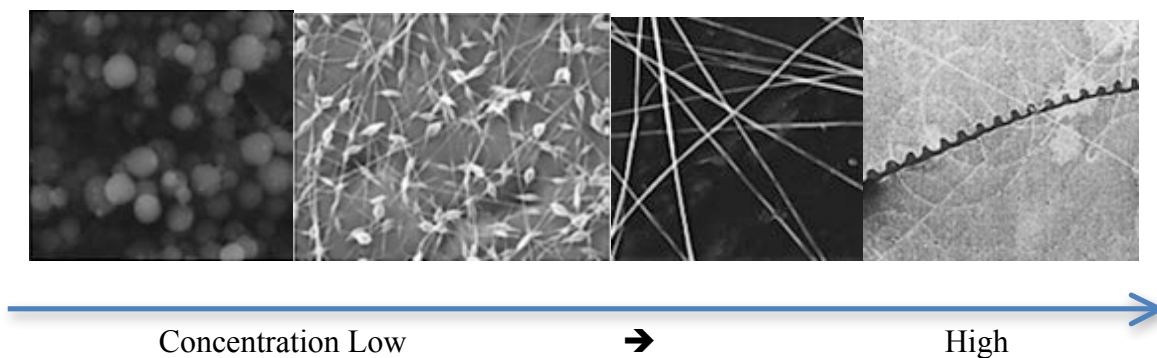
Figure 6 Effect of solution concentration on morphology (Lee, Kim et al. 2003) and (Yang, Li et al. 2004)

Molecular weight

Molecular weight shows how polymer chains elongate in solutions, which refer to solution viscosity. It has an impact on the morphology of electrospun fibers as well. When concentration is fixed and polymer molecular weight decrease, the spinning process tends to produce poor fibers and the formation of bead are favorable. In other words, fine fiber with no beads will be fabricated with a higher molecular weight. As molecular weight continue to increase, ribbons will form with diameters larger than nanoscale (Koski, Yim et al. 2004).

Viscosity

Solution viscosity is another key factor in electrospinning as it affects the fibers diameter and morphology greatly. Fabrication of nanofibers requires an appropriated viscosity neither too low nor too high, otherwise smooth nanofibers can't form.(Larrondo and St John Manley 1981). By changing of the concentration of the solution, viscosity can change; so nanofibers with different diameters and morphology can be produced. It is commonly known that polymer viscosity, concentration, and molecular weight are related to each other. When the viscosity is very low, beads show up and surface tension have the biggest influence on the morphology (Li

18

and Wang 2013). From above it suggests the fabrication of continuous fibers require an appropriate viscosity not too low or too high.

Surface tension

Surface tension, which is related to solvent in solution, greatly influence the electrospinning process (Dzenis 2004). Different solvents have different surface tensions. Low surface tension in the solution prevent beads forming, and high surface tension in the solution make bending jets unstable which result in series of problem occurring in electrospinning(Shin, Hohman et al. 2001). Low surface tensions, causing electric fields to decrease, would be very helpful for elctrospinng process (Haghi and Akbari 2007).

Conductivity

Several factors can change the solution conductivity such as polymer and solvent type, the ionic salt existence in the polymer system. Polyelectrolyte polymers make jet carry more charge than those without electrolyte group due to the existence of ions. After applying electric field, this cause the surface tension increase resulting in poor fibers producing (Allhoff, Lin et al. 2009). The mixing of ionic salts with the solution can increase the conductivity, which was reported of leading to form finer nanofibers (Narayan, Kumta et al. 2004). Besides, the using of organic acid as solvent could improve conductivity of solutions as well.

1.8.2 Processing Parameters

Voltage

Voltage is of importance on determining fiber size and morphology. As power supply

increase, the electrostatic repulsion increases causing more polymer ejection and the stress increase as well causing jet stretching. Higher voltage is favorable for making finer fibers due to the increasing electrostatic repulsion (Demir, Yilgor et al. 2002). Increasing voltage can extremely decrease the fiber size, and some studies show that the fibers size were reduce to half of their size by applying a voltage twice higher (Larrondo and St John Manley 1981). Even though high voltage contributes in decreasing fibers sized, it makes jet eject and spray to a wider area, bring difficulties in experiment control.

Flow rate

Taylor cone only formed when a suitable flow rate applied to processing. At very low flow rate Taylor cone will not formed due to the empty space in the needle and the spinning process would pause. At High flow rate solution may accumulate and block the needle, which could also cause the process to stop. Several experiments has been taken to study how flow rate influence nanofibers size and morphology (Zong, Kim et al. 2002). In general low flow rate is preferable in fabricating finer fiber and with solvent evaporated thoroughly (Yuan, Zhang et al. 2004). Also, flow rate can affect charge density on the jet surface, which result in fiber size and morphology changing. The rate of charge removal reflects the balance of ion forming and transporting rate of the in the jet needle. The lower flow rate results to more accumulation of ions in the jet and improve the chances to boost the surface charge density. On the contrary, Needle holds the solution less time, therefore less chances for ions, in contact under faster flow.

Collectors

Generally, the substrate as the target of the projected nanofibers acts as a sample holder and conductor in electrospinning process. Aluminum foil is usually applied as a collector, but for

variety of the applications, the re-shaped collectors, such as wire mesh, pin, grids rotating rods, etc., can better accommodating the need of further procedure or get rid of the fiber transfering problem.

Working distance

Working distance is the distance between the tip of syringe and the target substrate. In spite of the fact that distance elongation can introduce and add bending instabilities, and also promote the whipping action benefiting the fine fabrication of product polymer, it has to strike a balance with the intensity of electric field which is exponentially dropping with widening of the gap. Otherwise, it is conceivable that an insufficient surface charge density attribute to the gap distance can compromise the electrostatic force thereby, in reverse, deactivating and rejecting those effects mentioned above (Pena 2009).

1.8.3 Ambient Parameters

In addition to the mentioned above, the morphology property of the electrospun nanofibers is also sensitive to temperature, humidity, etc (Huang, Zhang et al. 2003). For instance, there exist a negative relationship between fiber diameters and temperature that is within "friendly range", since the temperature varies solution viscosity inversely. In other words, the higher temperature exerts a lower viscosity that impedes the thickening of fibers. For humidity, rapid charge neutralizing, thereby attenuating of stretching force, due to high density of polar water molecules will give rise to the thick fibers. In contrast, Low humidity may accelerate the solvent evaporation, eventually to affect the fiber morphology.

2.1 Chemicals Used

In this experiment, PVP/Cu^{2+} composite nanofibers were prepared by electrospinning. PVP nanofibers were used as reference in the experiment. The chemicals used in the experiment are listed in Table 3.

Table 3 Chemicals used in the fabrication of PVP nanofibers and PVP/Cu^{2+} composite nanofibers

Chemical	Formula	Molar Mass(g/mol)	Density(g/cm^3)	Company
Polyvinylpyrrolidone	$(C_6H_9NO)_n$	2.5	1.2	Sigma-aldrich
Copper(Ⅱ) Nitrate Trihydrate	$Cu(NO_3)_2 \cdot 3H_2O$	241.60	3.05	Sigma-aldrich
Ethyl Alcohol	CH_3CH_2OH	46.06	0.789	Pharmo-Aaper

2.2 Electrospinning Solution

Four groups of identical PVP solution (8%wt) were prepared by dissolving 0.8g PVP(M_n=1300 000) powders into 10ml ethyl alcohol. The solutions were contained in four vials

and ultrasonicated for 1 hour. $Cu(NO_3)_2 \cdot 3H_2O$ powders of different weight(0.017, 0.026, and 0.052g) were added to three vials of PVP solution and marked Ⅰ,Ⅱ,Ⅲ respectively. All of the four groups were ultrasonicated for about 5 hours at room temperature to form transparent homogenous solutions. Therefore, PVP solution, PVP/Cu^{2+} I (weight ratio of $PVP:Cu(NO_3)_2=60:1$), Ⅱ ($PVP:Cu(NO_3)_2=40:1$), and Ⅲ ($PVP:Cu(NO_3)_2=20:1$) composite solution were obtained. These solutions were used in fabricating PVP nanofibers and PVP/Cu^{2+} (Ⅰ,Ⅱ,Ⅲ) composite nanofibers.

2.3 Electrospinning Condition

The electrospinning setup for this experiment is composed of syringes with stainless needles, a metering pump, a high voltage supply with two electrodes, and a collector. Those four groups of ultrasonicated solution were loaded into 10ml plastic syringes respectively. The needles used in this experiment were 20 gauge stainless needles. Once the solution loaded, the syringe was connected to Kd scientific metering pump, which can push the fluid out of the syringe needle at a constant flow rate. Syringe size, dispense volume and dispense flow rate were set before the experiment. A Gamma High Voltage Power Supply was utilized to provide an electric field with the emitting electrode connected to the syringe needle and the ground electrode connected to the collector. The collector was already covered with an aluminum foil sprayed with Teflon. Teflon was only applied to make the electrospun nanofibers get off the foil easily. The collector was placed at a fixed distance from the syringe needle.

After all the preparation above, metering pump and power supply were turned on to perform electrospinning. Applied voltage, flow rate, and working distance were adjusted till jet

sprayed out of the needle and uniform electrospun fibers collected on the collector screen. After a few adjustments, parameters were fixed. PVP and PVP/Cu^{2+}(I , II , III) nanofibers were prepared by electrospinning under the same condition as shown in Table 4.

Table 4 Processing parameters used in the electrospinning for all nanofibers

Voltage (KeV)	20
Flow Rate (ml/min)	0.045
Working Distance (cm)	18

In the electrospinning process, sometimes the dried jet clog and may block the needle causing the fibers forming inconstantly. So it's important to check the needle and remove the clog in time. When electrospinning was done, fibers were peeled off the aluminum foil and put into a vial. The vial was preserved in a vacuum desiccator for characterization.

CHAPTER 3 CHARACTERIZATION TECHNIQUES

3.1 Scanning Electron Microscopy (SEM)

The scanning electron microscopy(SEM) is a powerful technique to reveal the surface topography and chemical composition of materials. It can provide high-resolution images of sample surfaces by using a focused beam of electrons. The instrument used is LEO 1550 SEM as shown in Fig 7. The microscope is composed of an electron source(gun), electron lenses, detectors for signals, and display devices. The electron source produces a beam of electrons at the top of microscope. The electron beam become accelerated and goes through the column of the microscope. Electromagnetic lenses in the column can focus the electron beam into a smaller beam on the sample. When the beam strikes the surface of a solid sample, electrons interact with the atoms in the sample generating multiple signals. The signals containing the information of the sample can be collected by detectors and send to the display device.
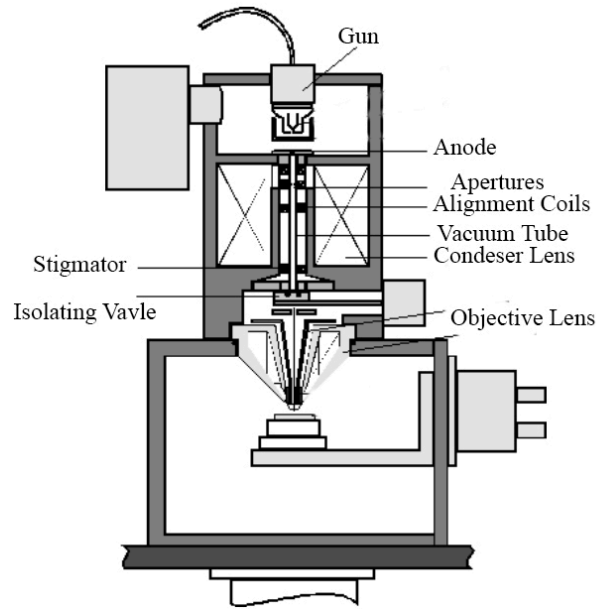
Figure 7 Schematic view of SEM vacuum column (SEM LEO 1550 MANUAL)

The most common used signals in SEM are secondary electrons(SE) and back scattered electrons(BSE). SE are low-energy electrons produced by inelastic scattering when an incident beam excites the electrons in the sample and loses most of its energy. BSE are high-energy electrons by elastic scattering when an incident beam interacts with a sample atom's nucleus with little energy loss. SE are sensitive to the surface of samples and typically used to reveal the morphology and topography. BSE are sensitive to the composition of samples images and commonly used to show the information of different elements of the sample.

3.2 Energy Dispersive X-Ray Spectroscopy (EDS)

The Energy Dispersive X-Ray Spectroscopy(EDS) is a quantitative microanalysis technique using characteristic x-rays generated by electron beam to identify the elemental composition of materials. It usually combines with other technique such as SEM. When a beam

of electrons hits the sample producing secondary electron, it leaves vacancies in the electron shells. Electron from higher state will fill these electron vacancies, emitting x-ray with characteristic energy and wavelength. Signals collected by the detector will be processed to create spectrum of x-ray energy vs. counts. By identifying lines in the spectrum, elemental composition of the sample can be obtained. It can identify almost all of the elements except for H, He, Li, and Be in the periodic table. EDS can give elemental mapping as well, which is very useful in viewing element distribution in the sample.

3.3 Ultraviolet-visible Spectroscopy(UV-vis)

The UV-vis spectroscopy is a straightforward technique used in analytical chemistry. It can measure the intensity of a beam after it passing through a sample. As shown in Fig 8, typically the spectrometer is composed of a light source, a diffraction grating, and a detector. Diffraction grating converts an ultraviolet light or a visible light into different wavelength light. Sample intensity, which the monochromatic beam passes through a cuvette containing a sample in the solvent, is defined as I_0. Reference intensity, which the beam passes through a cuvette containing only the solvent, is defined as I. The spectrometer used in this experiment is a single beam instrument, so I_0 must are measured by removing the sample. All the monochromatic beam of different wavelengths will be scanned by the spectrometer automatically.
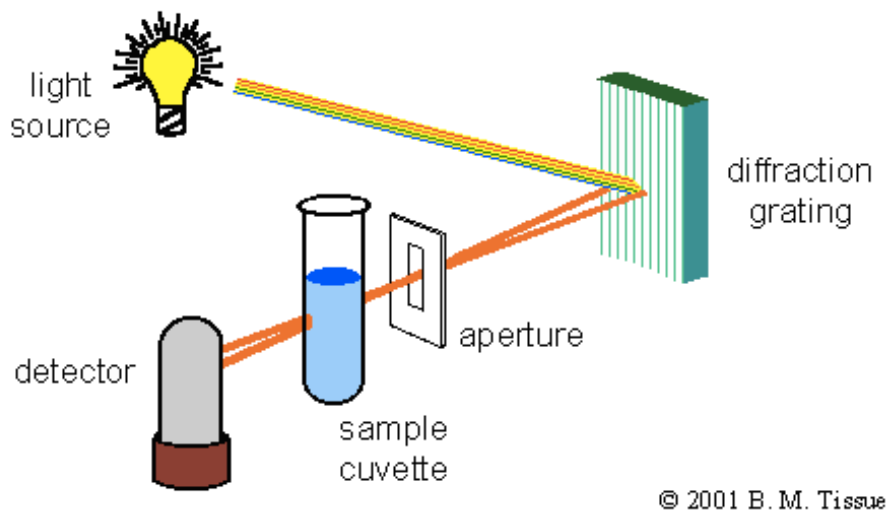
Figure 8 UV-vis absorbance spectroscopy setup (solution) (2001 B.M Tissue)

3.3.1Absorbance Spectrum

Absorbance spectrum is to measure how much the light is absorbed by a sample. The spectrometer used in this study is Spectra Suite by Ocean Optics. Absorbance (A) can be obtained according to the equation below.

Equation 2 Absorbance measurement (SpectraSuite Installation and Operation Manual, Ocean Optics, Inc)

$$A=-\log_{10}\left(\frac{S-D}{R-D}\right)$$

3.3.2Transmittance Spectrum

Transmission is the measurement of how much light passing through a sample relative to that passing through a reference. Transmission is expressed in percentage (%T) relative to a standard substance. Transmittance percentage %T can be calculated according to the equation below.

Equation 3 Transmittance measurement (SpectraSuite Installation and Operation Manual, Ocean Optics, Inc)

$$\%T = \left(\frac{S-D}{R-D}\right) \times 100\%$$

Where: S = Sample intensity at wavelength λ

D = Dark intensity at wavelength λ

R = Reference intensity at wavelength λ

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Color of the Electrospinning Solution and Electrospun Fibers

As mentioned above, PVP and PVP/Cu^{2+}(Ⅰ,Ⅱ,Ⅲ) electrospinning solutions were prepared. In Fig 9, there is a difference in color due to the different concentration of copper ions. Pure PVP solution is a colorless transparent fluid. PVP/Cu^{2+} solutions are changing from yellowish green to bluish green as Cu^{2+} concentration increase. Furthermore, the difference of viscosity can be observed. Pure PVP solution is most sticky and thick one among all the solutions. And the solution tends to be less sticky as Cu^{2+} ions increase. It has been reported that the addition of copper(Ⅱ) could greatly inhibit the polymerization of vinyl monomers (Braun 2010). Thus the presence of copper salts in the PVP/Cu^{2+} system could lead to a decreased viscosity.
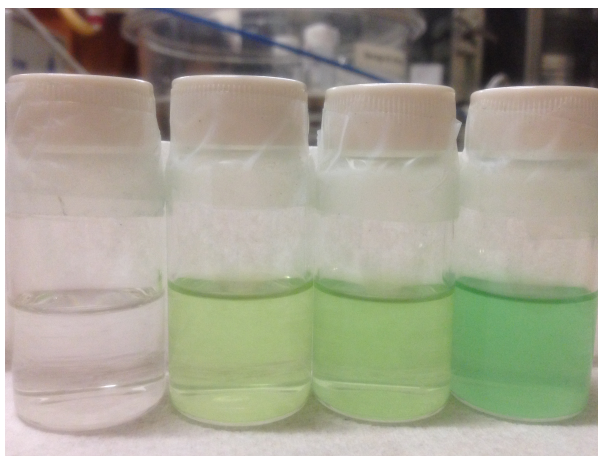
Figure 9 Ultrasonicated electrospinning solutions (a) PVP; (b) PVP/Cu^{2+}(I); (c) PVP/Cu^{2+}(II); (d) PVP/Cu^{2+}(Ⅲ)

PVP and PVP/Cu^{2+}(I , II ,III) fibers are synthesis by electrospinning. The colors of the fibers are not as strong as their corresponding solutions. But still there is a color difference between the fibers. In Fig 10, PVP fibers show a pure white color, PVP/Cu^{2+} composite fibers are from very light yellowish green to light bluish green as the concentration of copper salt increase.

Figure 10 Eletrospun fibers of (a) PVP; (b) PVP/Cu^{2+}(I); (c) PVP/Cu^{2+}(II); (d) PVP/Cu^{2+}(III)

4.2 Characterization with SEM and EDS

To observe the morphology of the fibers and study the effect of copper salt on the fiber, SEM images were taken. A piece of aluminum foil with fibers on it was cut off after electrospinning. Then it was placed on an aluminum substrate and coated with a layer of gold before SEM.

Fig 11 are images of electrospun PVP/Cu^{2+}(II) nanofibers at different magnification. Both of them were taken at same working distance, EHT, and using the same signal. Fig. 11 (a) shows the image of electrospun PVP/Cu^{2+} fibers at 10KX magnification, and Fig. 11 (b) shows

at 100KX magnification. It can be seen the composite nanofibers were electrospun uniformly with random orientation. Copper salt were successfully incorporated into polymer fibers. No beads showing on the images suggest that the parameters of electrospinning are suitable. The average diameters of the PVP/Cu^{2+}(Ⅱ) electrospun nanofibers on the image are at approximately 200-300 nm.

(a)

Mag = 100.00 K X   200nm   File Name = 040414-012.tif   Signal A = RBSD   Date :4 Apr 2014
WD =   7 mm   EHT = 20.00 kV   Time :13:56:03
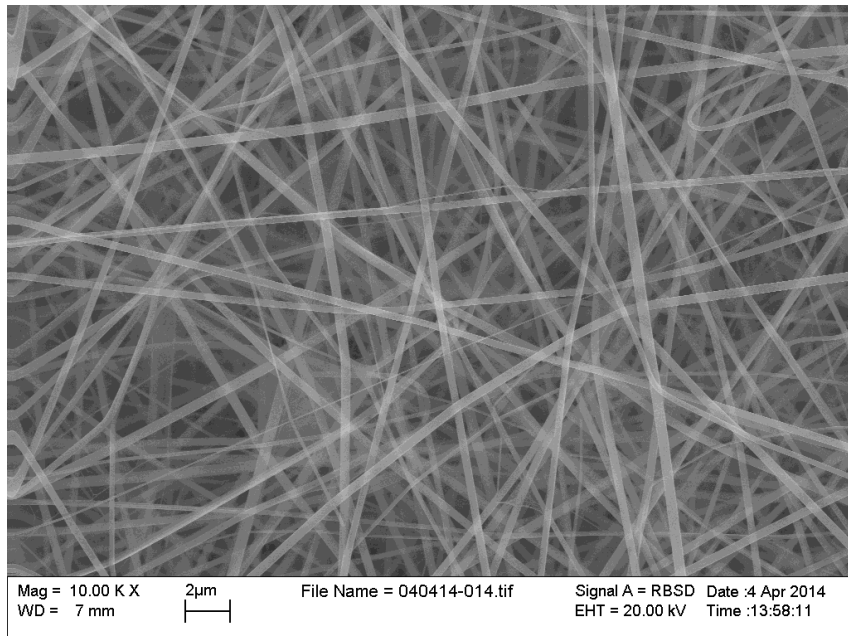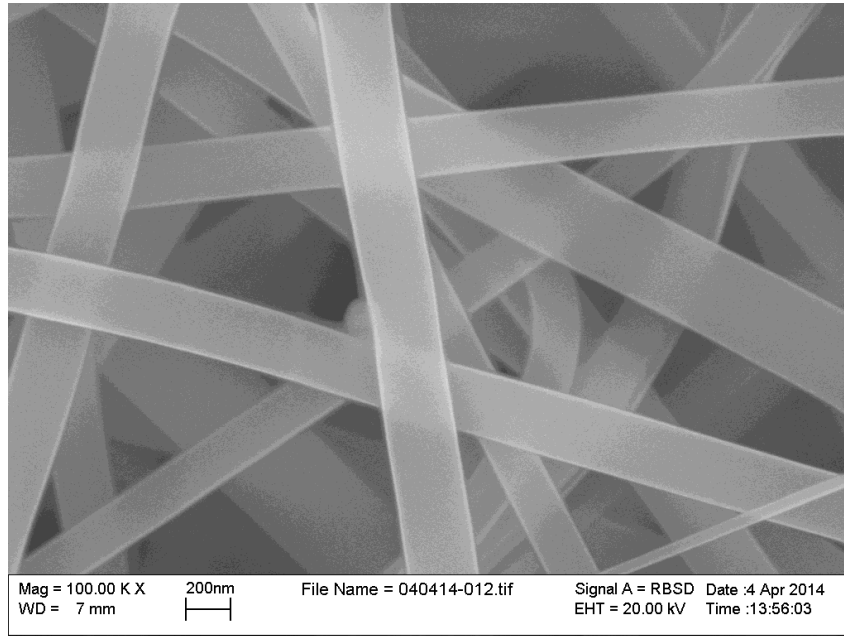
(b)

Figure 11 SEM images of PVP/Cu^{2+} naofibers(II) at (a) Mag=10.00KX and (b)Mag=100.00KX

Fig 12 is the EDS image of PVP/Cu^{2+}(II) electrospun naofibers. It confirmed the existence of copper in the polymer system even though the concentration is comparably low. The peaks of C and O are assigned to elements of PVP. And the peak of Al refers to the aluminum foil for holding the fibers. Elemental mapping were not used due to the low concentration of copper.
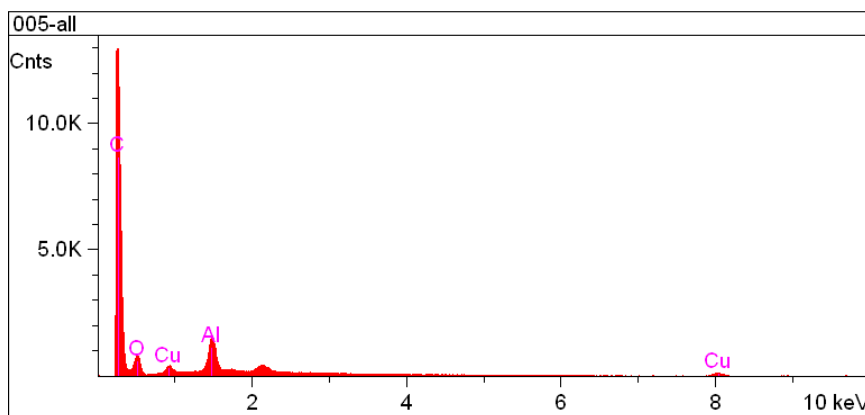
Figure 12 EDS spectrum of PVP/Cu^{2+} nanofibers on Aluminum substrate

Fig 13 are SEM images of different samples under the same working distance, EHT, and magnification and using the same signal. Fig (a) is the image of pure PVP fibers;(b) is PVP/Cu^{2+}(I) nanofibers;(c) is PVP/Cu^{2+}(II) nanofiebrs and (d) is PVP/Cu^{2+}(III) nanofibers. It can be seen that no significant difference of morphology between PVP nanofibers and PVP/Cu^{2+} nanofibers. They are uniform fibers down to nanoscale with random directions. PVP nanofibers have an average diameter ranging from 400-900nm. PVP/Cu^{2+} composite nanofibers(I , II ,III) show a noticeable decreased fiber size. Furthermore, as the concentration of Cu^{2+} increase, the average diameter of fibers tend to decrease slightly except for some fiber with sized not distributed evenly on Fig. 13 (d).

| Mag = 30.00 K X | 1µm | File Name = 032014-001.tif | Signal A = RBSD | Date :20 Mar 2014 |
| WD = 7 mm | | | EHT = 20.00 kV | Time :14:13:42 |

(a)

| Mag = 30.00 K X | 1µm | File Name = 040414-009.tif | Signal A = RBSD | Date :4 Apr 2014 |
| WD = 7 mm | | | EHT = 20.00 kV | Time :13:49:15 |

(b)

| Mag = 30.00 K X | 1µm | File Name = 040414-013.tif | Signal A = RBSD | Date :4 Apr 2014 |
| WD = 7 mm | | | EHT = 20.00 kV | Time :13:57:08 |

(c)

| Mag = 30.00 K X | 1µm | File Name = 040414-024.tif | Signal A = RBSD | Date :4 Apr 2014 |
| WD = 8 mm | | | EHT = 20.00 kV | Time :14:17:06 |

(d)

Figure 13 SEM images of (a) PVP nanofibers; (b) PVP/Cu^{2+}(I) nanofibers; (c) PVP/Cu^{2+}(II) nanofibers; (d) PVP/Cu^{2+}(III) nanofibers

4.3 UV-vis Spectroscopic Analysis

UV-vis was utilized to obtain the absorbance spectrum of electrospinning solutions and electrospun fibers. Transmittance spectrum of PVP/Cu^{2+}(II) nanofiebrs was tested as well.
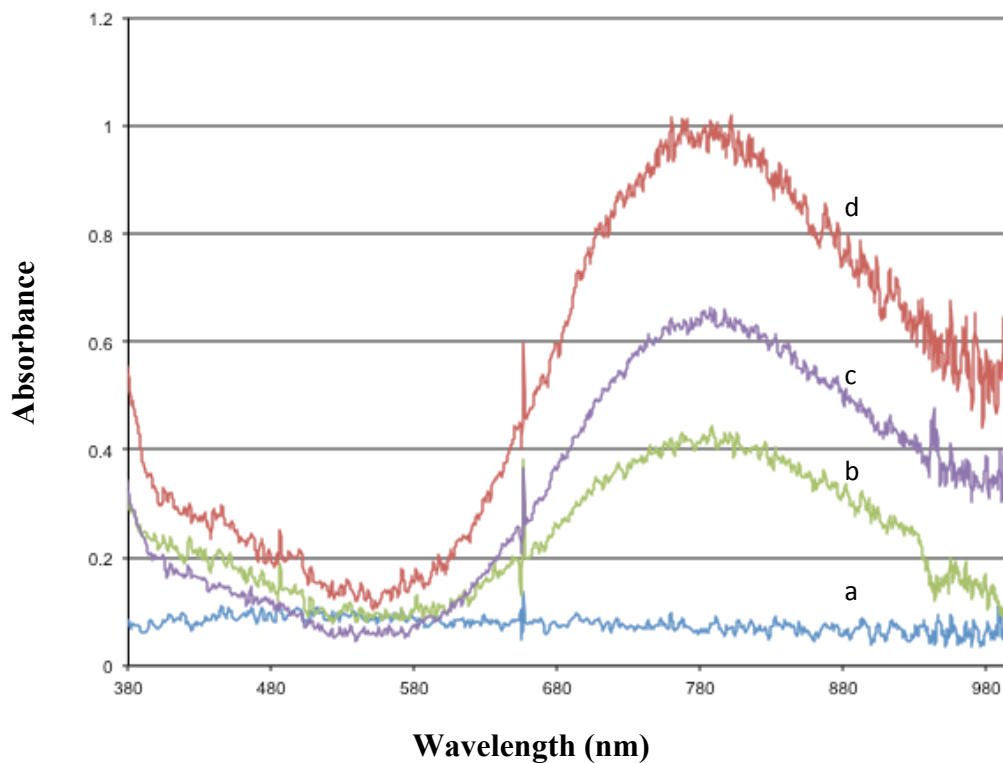
Figure 14 UV-vis absorbance spectrum of (a) PVP; (b) PVP/Cu^{2+}(I); (c) PVP/Cu^{2+}(II); (d) PVP/Cu^{2+}(III) solution

In Fig 14, PVP solution shows no characteristic band. All the PVP/Cu^{2+} solutions show a board band from 580-980nm. And as concentration of copper ion increase, the intensity of absorbance increased. The bands are assigned to d-d transition of Cu. The energy levels of copper d orbitals were split by coordination with PVP. The electron stayed in ground state jumped to the vacancy in excited state after absorbing photon with a specific wavelength.
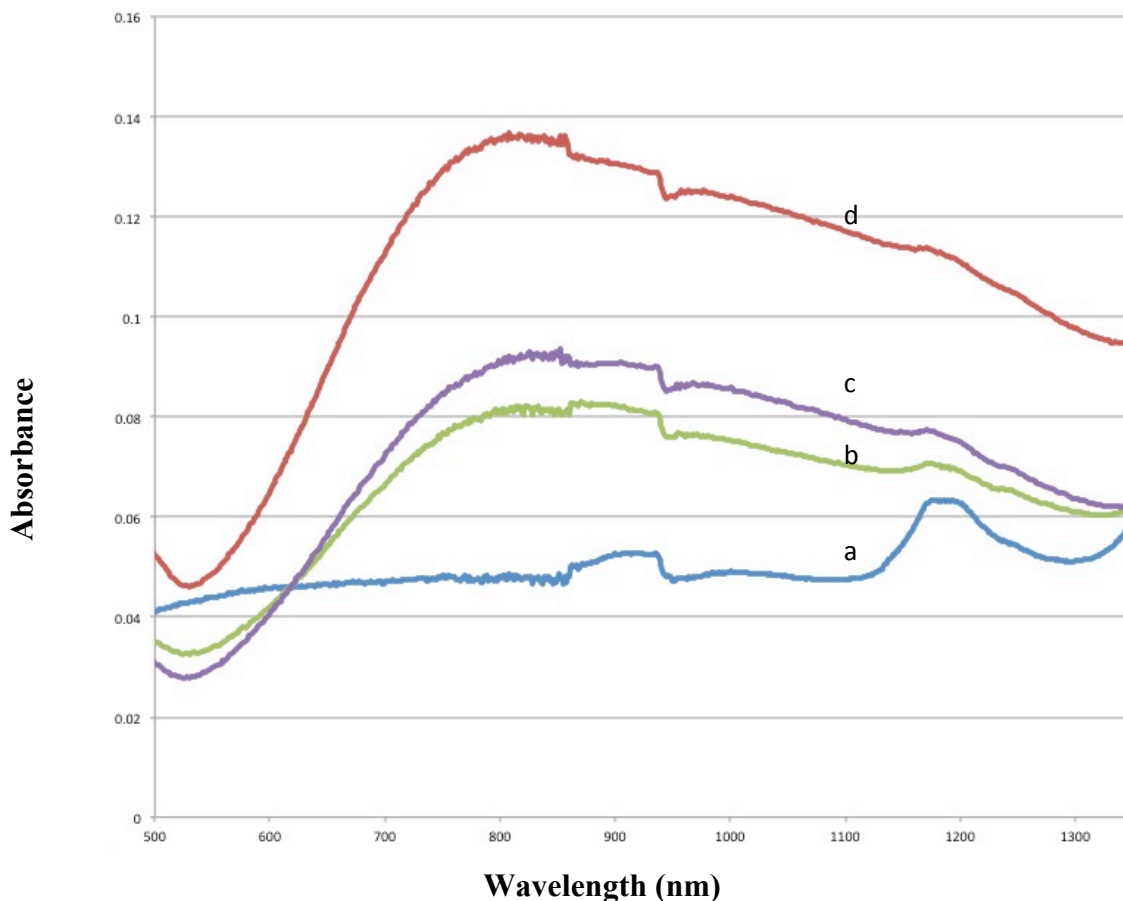
Figure 15 UV-vis absorbance spectrum of (a) PVP; (b) PVP/Cu^{2+}(I); (c) PVP/Cu^{2+}(II); (d) PVP/Cu^{2+}(III) electrospun nanofibers

Fig 15 is the absorbance spectrum of PVP nanofibers and PVP/Cu^{2+} nanofibers. It generally match the result form Fig 14. PVP hasn't shown any characteristic band except for some small peaks. All of the PVP/Cu^{2+} nanofibers have a board band at 550-1000nm. As concentration of copper ions increase, the light absorbance intensity increases. This suggests that the optical properties were improved by doping with copper salt, and the concentration of copper ions affect the light absorption intensity.
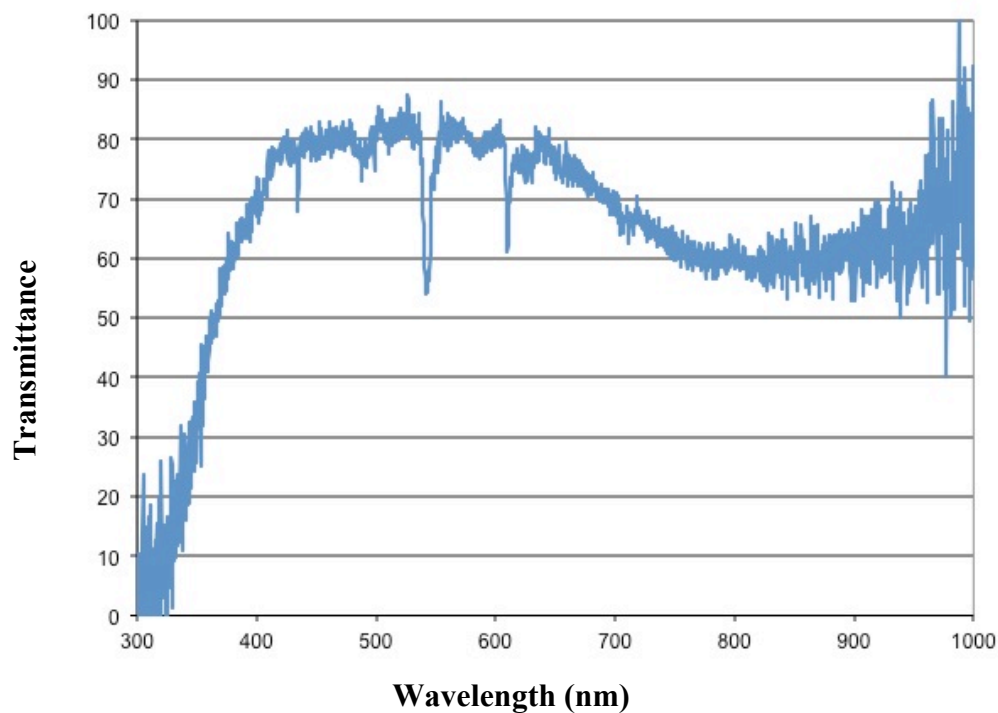
Figure 16 UV-vis transmittance spectrum of PVP/Cu^{2+}(II) nanofibers

For application as optical limiter, transmittance of light seems important as well. Transmittance is a percentage of light transmitting relative to the reference. The reference used in this experiment is air. As result shown in Fig 16, the greatest transmittance shows at 400-600 nm approximately. Together with Fig15 it may suggest that PVP/Cu^{2+} have the capability to absorb the light at specific wavelength(780nm) in IR region and let light at wavelength around 550nm pass.

CHAPTER 5 CONCLUSIONS

PVP nanofiber and PVP/Cu^{2+} nanofibers of different copper salt concentration was successfully fabricated by electrospinning. SEM images show the average diameter was about 200-900 nm, and the diameters of PVP/ Cu^{2+} nanofibers decrease after adding copper salt into the polymer matrix. UV-vis spectroscopic analysis indicates that PVP nanofibers don't have characteristic light absorption band however doping with copper salt make it have light absorbing ability. It conclude that PVP/Cu^{2+} may have a potential to be used as optical limiter.

CHAPTER 6 FUTURE WORK

Current work focused on preparing PVP/Cu^{2+} naofibers and study of their optical property mainly in light absorption ability. In the futher, emission spectrum may be taken to understand the optical properties of PVP/Cu^{2+} further. Structural and thermal properties may be studied as well.

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