ALIGNED AND ORIENTED POLYANILINE NANOFIBERS: FABRICATION AND APPLICATIONS

DISSERTATION

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By

Nan-Rong Chiou, B.S., M.S.

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The Ohio State University
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Dissertation Committee:
Professor Arthur J. Epstein
Professor L. James Lee
Professor Kurt W. Koelling

Approved by

Advisor
Graduate Program in Chemical Engineering
ABSTRACT

Polymers that conduct electricity are of interest for both fundamental science and many technologies. Polyaniline was the first discovered conducting polymers with the first report of its existence being in 1842 in the *Journal of Colorists and Dyists*. Study of the sludge at the bottom of the dye tanks was promoted because of the importance of aniline based dyes for the textile and carpet industries. However, it was not until 140 years later, in the mid-1980s, that the chemical and electrical properties of polyaniline were explored. Initially polyaniline was made as a powder. In the late 1980s it was discovered how to prepare forms of polyaniline that were soluble in a variety of solvents and could form films. This leads to broad application of this polymer in areas ranging from elimination of electrostatic charge, to anticorrosion coatings for ferrous alloys, to electron beam resists, to electrodes for light emitting displays, as well as many others.

In the past three years polyaniline nanofibers have attracted much attention in the field of nanotechnology. A wide variety of methods have been reported to prepare polyaniline nanofibers via the routes based on chemical oxidative polymerization. For examples, hard templates, surfactants, electrospinning, interfacial polymerization, seeding polymerization and rapid-mixing reaction all produce polyaniline nanofibers. However, these above methods are complicated and expensive means to obtain
nanofibers in one or multiple steps. Further, it is almost impossible to synthesize large arrays of aligned and oriented nanofibers of polyaniline and its derivatives via those methods. Therefore, it is of interest to introduce an easy, inexpensive, environmentally friendly and scalable one-step method to produce highly pure, uniform large arrays of aligned and oriented nanofibers as well as ordered nanofibers.

In this thesis, two novel, simple, and scalable techniques (called “dilute polymerization”, and “porous membrane controlled polymerization (PMCP)”) to control the formation of the aligned and ordered nanofibers (or nanowires) of polyaniline and its derivatives are reported. Through appropriate synthesis conditions, there are nearly ~100% of nanofibers formed in the bulk solution and of large arrays of aligned and oriented nanofibers formed on the surfaces of the substrates.

For polyaniline nanofibers formed in the bulk solution, the diameters of nanofibers ranging from 20nm to 250nm are tunable via the selection of polymerization conditions. The lengths vary from sub-micrometers to several micrometers. A single nanofiber can be easily isolated from the agglomeration. X-ray diffraction patterns show that doped polyaniline nanofibers are substantially crystalline.

Thin films deposited on a variety of substrates of various sizes shows highly uniform aligned and oriented polyaniline nanofibers that are perpendicular to the substrates. Those aligned and oriented uniform nanofibers have the tips ranging from 20nm to 40nm.

UV/vis spectra of polyaniline nanofibers formed in the both bulk and substrates are consistent with nonfibrous polyaniline powders prepared by the conventional
chemical synthesis. The nanofibrous morphology has no significant change when redoped/dedoped multiple times by the acid/base solutions. The formation mechanism of the nanofibers is discussed. Moreover, molecular modification of polyaniline nanostructures is also mentioned, thereby allowing preparation of nanofibers of a wide variety of polyaniline nanofibers and also control of the chemical, processing and electrical properties.

Finally, polyaniline nanostructures offer wide, exciting and interesting applications, such as DNA stretching, surface modification (e.g. superhydrophilicity and superhydrophobicity), etc.
Dedicated to

my wife, Sau Ha (Sarah);

to my parents;

and to my sisters.
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VITA

October 16, 1973  Born – Nantor, Taiwan

1996  B.S. Chemical Engineering, Tunghai University, Taiwan

1998-2000  Research Assistant, Institute of Chemistry, Academia Sinica, Taipei, Taiwan

2000-2002  M.S. Chemical Engineering, The Ohio State University

2002-2005  Graduate Teaching Assistant, Research Assistant, The Ohio State University

2005-present  NSEC Fellow The Ohio State University

PUBLICATIONS


Major Field: Chemical Engineering
  Chemistry
  Physics
  • Synthesis and characterization of conducting polymers. Prof. Arthur J. Epstein
  • Process for conducting polymers. Prof. L. James Lee
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CHAPTER 1

INTRODUCTION

Polyaniline is one of a class of conductive polymers, which can be synthesized through either chemical polymerization\textsuperscript{[1.1-1.5]} or electrochemical polymerization\textsuperscript{[1.2,1.6-1.8]}. Polyaniline is conventionally prepared by polymerizing an aniline monomer. The nitrogen atoms of monomer units are bonded to the para-carbon in the benzene ring of the next monomer unit. In chemical preparation, bulk polymerization is the most common method to prepare polyaniline. As reported previously\textsuperscript{[1.1-1.5]}, conventional bulk chemical synthesis produces irregular shaped polyaniline. There have been recent reports of a variety of other chemical methods used in order to obtain polyaniline nanofibers. These approaches include use of templates\textsuperscript{[1.9-1.14]} or surfactants\textsuperscript{[1.15-1.17]}, electrospinning\textsuperscript{[1.18-1.20]}, coagulating media\textsuperscript{[1.21,1.22]}, interfacial polymerization\textsuperscript{[1.23-1.28]}, seeding\textsuperscript{[1.29]}, and oligomer-assisted\textsuperscript{[1.30]} polymerization. Among these above methods, interfacial polymerization is an easier and less expensive means to obtain nanofibers in one step. However, this method requires organic solvents to dissolve the aniline monomer resulting in a waste stream that must be treated. Therefore, it is of interest to introduce an easy, inexpensive, environmentally friendly and scalable one-step method to produce highly pure, uniform
nanofibers with controllable average diameters ranging from 20nm to 250 nm in bulk quantities to meet the requirements for potential use on cell culture, electronic devices, sensors, biosensors, supercapacitors, hydrogen storage, etc.

According to the classical theory of nucleation and growth,[1,31,1,32] the mechanism of nucleation followed by growth is responsible for polyaniline morphology. An elongated form (e.g., fibers, tubes or rods) is established as the growth rate for polyaniline is distinctly not identical in all directions (anisotropic growth).[1,31,1,32] Moreover, new active nucleation centers could be formed on initially formed nanofibrils for additional growth of nanofibrils resulting in a branched network or dendrites (secondary nucleation).[1,31,1,32] If the reduced concentrations of monomer and/or oxidant are used or the concentrations of monomer and/or oxidant are careful controlled in the initial stage of polymerization, polyaniline may form in favor of 1-D nanostructures exclusively. Following this route, herein, two novel, facile methods were introduced for the first time to synthesize polyaniline nanofibers and aligned polyaniline nanofibers.

In this thesis I report two simple approaches to synthesize polyaniline nanofibers in an aqueous solution without aid of specific templates, such as surfactants, large organic dopant acids, organic solvents, nanoscale seeds, oligomers, etc. In the first approach (called dilute polymerization), polymerization needs to be carried out in dilute aniline in the presence of the protonic acid. This contrasts with the relatively high concentrations of aniline used to synthesize polyaniline powders in the conventional polymerization.[1,1-1,5] We present here the first study of the morphology of polyaniline precipitates that result from the polymerization in dilute aniline solution as we describe in
the experimental section. We use the term “dilute aniline” here to describe the polymerization of aniline being carried out at a substantially lower concentration of aniline, e.g. less than ~0.01M, compared to the one used in the conventional synthesis, e.g. ~0.4M of aniline from Ref. [1.4]. In addition, the molar ratio of aniline to oxidant in dilute aniline is used in the range of 1 to 4.35 for materials reported here. This contrasts to the fixed molar ratio of aniline to oxidant of 4.35 in the conventional synthesis. In fact, the molar ratio has a very small effect on the nanofibrous morphology. In the second approach (called porous membrane controlled polymerization), a permeable tubing or membrane is used to steadily control the release of aniline monomer into an oxidant solution (or vice versa) in the protonic acid media to architect polyaniline nanostructures. After polymerization, polyaniline nanofibers are collected directly outside the tubing or inside the tubing without any further treatment to obtain free-standing nanofibers.

In addition to the nanofibers formed in the bulk solution, aligned and molecularly ordered polyaniline nanofibers (or nanowires) also can be found simultaneously on the substrates (e.g. the wall of the beaker, the interface between air and reaction solution, solid materials, stirring magnetic bar, etc.) present in the reaction mixture using either dilute polymerization or porous membrane controlled polymerization. It was earlier reported that a thin film of polyaniline can be deposited on a variety of substrates of various sizes in the conventional polymerization of aniline, called in-situ adsorption polymerization.[1,33] However, the deposited thin films prepared by the conventional chemical polymerization are only composed of the irregularly granular particulates.[1,29,1,34-1,36] Until now, aligned and oriented nanostructures of polyaniline are
generally produced by chemically or electrochemically polymerization through the assistance of the hard templates. In the hard-template polymerization, polyaniline is confined to grow inside the channels of the membranes. After polymerization, the templates have to be removed or etched away carefully to obtain an oriented nanostructured thin film. This process sometimes results in the collapse or destruction of the aligned nanofibers. In addition, the diameter of the aligned nanofibers is limited by the pore size of the template membrane used. Recently, a step-wise electrochemical deposition process was introduced to deposit oriented polyaniline nanofibers on the conductive substrates (e.g. Au, Pt etc.) without using the hard template. This method is facile to produce aligned polyaniline nanofibers but limited to the conductive substrates.

For template or step-wise electrochemical deposition methods, a very large uniform array of aligned and oriented nanostructures (e.g. a letter sized array, 8.5 inches x 11 inches) is mostly impossible to be fabricated. Those limitations restrict the applicability of the aligned nanofibers, especially for the usages of the surface response (superhydrophobic or superhydrophilic surfaces), electrodes for organic or polymeric light-emitting diodes, field-emission display, DNA stretching, chemical sensors, biosensors etc.

We have successfully coated aligned and oriented nanofibers (or nanowires) of polyaniline and its derivatives onto a very wide variety of substrates including poly (ethylene terephthalate) (PET), Poly (methyl methacrylate) (PMMA), polystyrene (PS), Poly (dimethyl siloxane) (PDMS), Teflon®, paper, glass, ITO, and Si wafer in a wide
variety of sizes using either *dilute polymerization* or *porous membrane controlled polymerization*. There is no apparent difference between those two methods for the morphology of the surfaces coated by the aligned nanofibers on the conductive (e.g. ITO substrates, Si wafer, etc.) or inert substrates (e.g. glass, PET, PMMA, PS, PDMS, Teflon®, etc.). The geometry (e.g. flat or hierarchical surfaces) of the substrates also has no significant effect on the coating. This shows that the two methods we propose here are very robust and this also leads to broad applications of this aligned and oriented nanostructure.
REFERENCES: CHAPTER 1


CHAPTER 2

BACKGROUND

2.1 CONDUCTIVE POLYMER

A conductive polymer, sometimes called conducting polymer, conjugated conductive polymer or organic polymeric conductor, is the organic macromolecule which has π conjugated double bonds where the overlapping π-electrons fairly extend and delocalize along the polymer backbone. Conductive polymers can provide the conduction of electric charges through movement of electrons in unoccupied energy states or movement of holes in filled energy states. These conductive holes and electrons arise from chemical oxidation or reduction, i.e. p-type or n-type doping. During the chemical oxidation or reduction, the conductive polymer is doped with anionic specie which is the electron acceptor, or with cationic specie which is the electron donor.\[2,1,2,2\] Therefore, it is important to understand the principle that conductive polymers can alternatively behave as a metal, semiconductor, or insulator. Free electron model is introduced first and extended in further to band model to comprehensively explain the properties of conductive polymers. Finally, chemical doping also is given to illustrate briefly the conductivity of conductive polymers.
2.1.1 Free Electron Model

The free electron model describes that valence electrons move freely through the volume of the metal. The forces are neglected between conduction electrons and the ion cores. As shown in figure 2.1, sodium cores with positive charge share the moving electrons with each other. The moving electrons come from 3s valence electron of sodium which has the electronic configuration $1s^22s^22p^63s$. Thus, sodium atomic cores ($\text{Na}^+$ ions) are dispersed in the sea of conduction electrons. However, this model fails to explain the difference between metals, semiconductors, and insulators, why some chemical elements crystallize to form good conductors, and why conductive polymers have the conduction of electrical charges. Therefore, band model is given here.

Figure 2.1: Schematic illustration of the free electron model applied to sodium metal.
2.1.2 Band Model

Based on the invention of quantum mechanics, the band model refines the previous model. It introduces that a band gap exists between the valence band and the conduction band. As shown in Figure 2.2, in metals conduction band overlaps the valence band. There is no evidence of the band gaps between them. Electrons can move freely in the conduction band. In semiconductors, the valence band and the conduction band are separated by enough small band gaps where electrons in valence band can jump to conduction band through thermal or optical excitation energy. In insulators, there exists a large band gap between the valence band and the conduction band.\textsuperscript{[2,3,4]}

Figure 2.2: Schematic band model.\textsuperscript{[2,3]}
The band model is also quite appropriate to explain why conductive polymers can be conductors, semiconductors, or insulators. Conductive polymers exhibit \( \pi \) conjugation where the overlapping \( \pi \)-electrons fairly extend and delocalize along a polymer backbone. As shown in Figure 2.3, the band gap can be decreased gradually by extending the \( \pi \) length of the molecules. A dimer has the largest band gap. In addition, a polymer can be as conductive as a metal when the band gap is removed, a semiconductor (e.g. silicon) when the band gap is small enough, or an insulator as polyethylene when the band gap is large.

![Figure 2.3: Schematic band model of \( \pi \) conjugated conductive polymer][2.85]
2.1.3 Doping

In a conductive polymer, electrons are removed (or added) by chemical methods to form positive (or negative) charge on the polymer chain. Also, negative (or positive) ions bond together to form polymer salt. This process is called “doping” by which the conductivity of conductive polymers can be increased to several orders of magnitude, such as polyacetylene doped with iodide ion. The conductivity of doped polyacetylene is 9 orders of magnitude higher than that of an undoped one.\textsuperscript{[2.1]} In a p-type conductive polymer, the concentration of holes in the valence band is greater than that of electrons in the conduction band. Most conductive polymers are p-type, such as polyaniline, polypyrrole, and polythiophene. However, n-type conductive polymers still can be found, such as poly (benzobisi-midazobenzophenanthroline) (BBL), in which the concentration of electrons in the conduction band is higher than that of holes in the valence band. In addition, some polythiophene derivatives can be doped n-type. Polyacetylene can be doped p-type or n-type. The schematic band diagram of p-type and n-type doped polymers is shown in Figure 2.4.
Figure 2.4: Schematic band diagram of p-type and n-type doped polymers\textsuperscript{[2,4]}
2.2 POLYANILINE

Polymers that conduct electricity are of interest for both fundamental science and many technologies. Polyaniline was the first discovered conducting polymers, with the first report of its existence being in 1842 in the *Journal of Colorists and Dyists*. Study of the sludge at the bottom of the dye tanks was promoted because of the importance of aniline based dyes for the textile and carpet industries. However, it was not until 140 years later, in the mid-1980s, that the chemical and electrical properties of polyaniline were explored. Initially polyaniline was made as a powder. In the late 1980s it was discovered how to prepare forms of polyaniline that were soluble in a variety of solvents and could form films. This leads to broad application of this polymer in areas ranging from elimination of electrostatic charge, to anticorrosion coatings for ferrous alloys, to electron beam resists, to electrodes for light emitting displays, as well as many others.

Polyaniline has three different allowed oxidation states.\[^{2.5}\] They are fully reduced form (leucoemeraldine), half oxidized form (emeraldine) and fully oxidized form (pernigraniline) as shown in Figure 2.5, respectively. In most cases, when polyaniline is prepared by the *conventional* chemical oxidative polymerization from aniline monomer in protonic acid, emeraldine salt which is “doped polyaniline” or “protonated salt form” (Fig. 2.6a) can be obtained.\[^{2.5-2.8}\] Emeraldine base (EB, undoped form) consists of alternating reduced and oxidized repeating units, i.e. benzoid (phenylene diamine) and quinoid (quinoid diimine) groups (Figs. 2.5b or 2.6b).\[^{2.6}\] Reversible switching between doped form and undoped form (i.e. emeraldine salt and base) can be achieved via protonation of imine nitrogen atoms of the quinoid group, forming an acid-base complex.
(Fig. 2.6a), for the base form, or deprotonation of the amine nitrogen atoms of the benzoid group for the salt form by protonic acids and base, respectively. This processing is called protonation since acids and bases neither reduce nor increase the number of electrons associated with the polymer chains as shown in Figure 2.6.\textsuperscript{[2,7]} As-synthesized polyaniline nanofibers prepared by dilute polymerization or porous membrane controlled polymerization are in the doped form since the polymerization is carried out in protonic acid media. We use dilute basic solution (0.1M NH\textsubscript{4}OH\textsubscript{(aq)}) to wash as-prepared polyaniline nanofibers resulting in the deprotonation of polyaniline backbones, simultaneously forming undoped polyaniline (emeraldine base). When undoped polyaniline is treated with a strong protonic acid again (e.g. 1M HCl\textsubscript{(aq)}), it changes back to the doped form. The doping, dedoping, and redoping are all reversible and have very little effect on the morphology of polyaniline nanofibers as prepared by dilute and/or porous membrane controlled polymerization. However, redoping and dedoping will change the degree of the crystalline of polyaniline since this processing alternates the arrangement of polyaniline chains. In fact, the properties of polyaniline are strongly affected by the processing including the use of solvents, temperature, dopants, etc.
Figure 2.5: Chemical structures of polyaniline (a) leucoemeraldine base (b) emeraldine base (c) pernigraniline.

Figure 2.6: Protonation (doping) and deprotonation (dedoping) of polyaniline (a) emeraldine salt (polaron) (b) emeraldine base. HA: protonic acid and OH-: base.
The conductivity of polyaniline is varied, depending on the degree of protonation (doping) of emeraldine base. Heavily doped polyaniline (often termed 50% protonation) corresponds to protonation of all imine nitrogen atoms of quinoid group resulting in the highest conductivity.\textsuperscript{[2.8]} In contrast, EB is unprotonated. The requirement to maintain the original conductivity of polyaniline in solutions is to protonate polyaniline with the desired concentration of acids and then, adjust pH of solutions with acids to keep the same pH with desired concentration of acids used for protonation of polyaniline, or alternatively to covalently bond counter ions into the backbone to form “self-doped” polyaniline.

2.3 NUCLEATION AND GROWTH

2.3.1 Thermodynamic Formulas for Both Nucleation and Growth of a Material

The driving force for nucleation and growth of one-component material in liquid solutions is the supersaturation $\Delta\mu$ (in Joules) defined as\textsuperscript{[2.9-2.16]}

$$\Delta\mu = \mu_l - \mu_p$$  \hspace{1cm} (eq. 1)

Where $\mu_l$ and $\mu_p$ are the chemical potentials of a molecule in the solution (l) and in the bulk of the solid phase (p), respectively.\textsuperscript{[2.10]}
When $\Delta \mu > 0$, the solution is supersaturated, as only then are nucleation and/or growth of the particle possible. The solution is saturated or undersaturated when $\Delta \mu = 0$ or $\Delta \mu < 0$, respectively.\[^{2.10}\]

Using known thermodynamic expressions for $\mu_l$ and $\mu_p$, one may present $\Delta \mu$ in the form e.g.,\[^{2.11}\]

\[
\Delta \mu = kT \ln S
\]

(eq.2)

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $S$ is the degree of supersaturation.

The work to form a cluster of molecules can be found by thermodynamic considerations, since it is defined as the difference between the free energy ($\Delta G$) (in Joules) of the system in its final and initial states, i.e. after and before the cluster formation. In reality, the work should contain an additional energy term accounting for the presence of an interface between the cluster and the ambient solution and for the difference of the cluster properties from those of the bulk solid. Thus, most generally, $\Delta G$ is written down as\[^{2.10}\]

\[
\Delta G = -\Delta \mu + \Phi
\]

(eq.3)

where $\Phi$ (in Joules) has the physical significance of effective excess energy of the cluster.
2.3.1.1 Thermodynamic Formulas for Homogeneous Nucleation

Homogeneous nucleation occurs in the volume of ideally pure solutions, i.e. solutions constituted of solvent and solute molecules only. According to the classical nucleation theory\cite{2.9-2.17}, the free energy of forming stable nuclei in the solution can be expressed as:\cite{2.10}

\[ \Delta G_{\text{HOMO}} = -kT\ln S + \sigma_{pl} A_{pl} \]

(\text{eq}.4)

Where \( \sigma_{pl} \) is the total interfacial energy between the particle (p) and the liquid (l), and \( A_{pl} \) is the surface area of the particle in contact with the liquid.

2.3.1.2 Thermodynamic Formulas for Heterogeneous Nucleation

Heterogeneous nucleation takes place in solutions containing impurity molecules and/or foreign microparticles or substrates that provide active centers for nucleation. According to the classic theory of nucleation and growth,\cite{2.9-2.17} the free energy of forming stable nuclei on a substrate is determined by four factors.\cite{2.9,2.15,1.16}

(i) \( S \): the degree of supersaturation

(ii) \( \sigma_{pl} \): the interfacial energy between the particle (p) and the liquid (l),

(iii) \( \sigma_{ps} \): the interfacial energy between the particle and the substrate (s),

(iii) \( \sigma_{sl} \): the interfacial energy between the substrate and the liquid.
\[ \Delta G_{\text{HETER}} = -kT \ln S + \sigma_{pl} A_{pl} \pm (\sigma_{ps} - \sigma_{sl}) A_{ps} \]  

(eq. 5)

where \( A \) is the surface area of the particle in contact with the liquid (\( A_{pl} \)) and the substrate (\( A_{ps} \)), \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature.

2.3.2 Homogeneous Nucleation

Homogeneous nucleation\(^{[2.9-2.18]}\) occurs in the volume of ideally pure solutions, \textit{i.e.} solutions constituted of solvent and solute molecules only. In homogeneous nucleation, the critical nucleus appears in the middle of the original bulk phase. Nucleation is an activated process, in which the barrier height (the free energy change to create the critical nucleus) varies from an infinite value to zero. Because of this exponential dependence on a rapidly change of free-energy barrier height, homogeneous rates are extraordinarily sensitive to thermodynamic conditions of temperature and pressure, as well as to small variations in intermolecular potentials. To achieve homogeneous nucleation, very careful attention is required to have high purity of samples and careful control experimental conditions. In the world outside the laboratory, homogeneous nucleation still occurs, but is relatively rare.

2.3.3 Heterogeneous Nucleation

Heterogeneous nucleation\(^{[2.9-2.18]}\) takes place in solutions containing impurity molecules and/or foreign microparticles or substrates that provide active centers for nucleation. Most nucleation occurs heterogeneously, with rates increased by many orders
of magnitude over homogeneous rates, due to the presence of impurities. One kind of heterogeneous nucleation occurs when the evolving nucleus forms around a single impurity molecule or ion, or around a tiny impurity that acts as a seed at the center of the nucleus. A second type of heterogeneous nucleation involves the formation of the new phase on a (nearly planar) surface of a different material. Such nucleation can occur on the walls of a container, e.g. dilute polymerization for polyaniline nanofibers,\textsuperscript{[2.19]} or on the surface of suspended particles, e.g. seeding polymerization for conductive polymer nanostructures\textsuperscript{[2.20]} that are large enough that their surface curvature does not play a role. The critical nucleus contacts the substrate (but does not surround) resulting in change of the symmetry from spherical to cylindrical in the simplest case.

2.4 INTERMOLECULAR FORCES: VAN DER WAALS FORCES

Intermolecular forces are the attractive forces exerted in the molecules. Intermolecular forces are the reason for gases to show the nonideal behavior. They exert even stronger influence in liquid or solid. For example, the kinetic energy of the water vapor molecules decreases as temperature drops in the system. Under a certain temperature, the molecules no longer break away from the attraction of each other. Thus, they tend to aggregate and form a small drop of liquid. This processing arising from the phase transition is called condensation.\textsuperscript{[2.21]}

Generally, there are different types of intermolecular forces among the molecules including dipole-dipole, dipole-induced dipole, and dispersion forces, which are also
commonly named as van der Waals forces.\cite{2.21} Dipole-dipole forces are electrostatic forces between polar molecules, which can be understood in terms of Coulomb’s law. The strength of the forces depends on the charge and size of the ion, and the dipole moment and the size of the polar molecule. Dipole-induced dipole forces are the attractive interaction between either an ion or a polar molecule and a non-polar molecule. Dispersion forces are the attractive forces resulting from the temporary dipoles induced in atoms or molecules. The strength of dispersion forces increases as the increase of molar mass or of atom sizes in which outer electrons are less bonded to nuclei and easy to be disturbed by neighboring molecules. Typically, van der Waals forces are weak, but present always, since their strength is inversely proportional to 7th power of the distance between two molecules. However, when the system is miniaturized to micro/nanoscale, e.g. 100nm in sizes, the van der Waals forces exert strong and effective influence at gas-liquid or liquid-solid interfaces.\cite{2.21-2.23}

2.5 SUPERHYDROPHILICITY AND SUPERHYDROPHOBICITY

2.5.1 Roughness Effect on Hydrophilic and Hydrophobic Surfaces

Surface modification has attracted much attention in the field of nanotechnology in the recent years. Wettability of the solid surfaces is governed by both surface energy and roughness or surface structures. The surface energy is the intrinsic property of each solid material dependent on the chemical composition. In general, a hydrophobic surface, in which the water contact angle is enhanced by small roughness and is higher than about
150°, is called "superhydrophobic", and a hydrophilic surface, in which the water contact angle is similarly reduced by small roughness and is less than 5°, is called "superhydrophilic".

Those phenomena can be explained by Wenzel equation (eq.6):[2.24,2.25]

$$\cos \theta = r \left( \gamma_{SV} - \gamma_{SL} \right) / \gamma_{LV} \quad \text{(eq.6)}$$

where $\gamma_{SV}$, $\gamma_{SL}$ and $\gamma_{LV}$ are the interfacial energies per unit area of the solid-gas, solid-liquid and liquid-gas, respectively, and $r$ is a roughness factor, which is defined as the ratio of the actual area of the rough surface to the geometric projected area and is always larger than 1. Therefore, from equation (6), we know that the roughness of the substrates can enhance both the hydrophobicity of the hydrophobic surfaces and the hydrophilicity of the hydrophilic surfaces as shown in Figure 2.7. In addition, Cassie et. al. assumed that the air is superhydrophobic with a water contact angle of 180°. They claimed that air trapped on the surfaces may enhance the hydrophobicity. Thus, they proposed equation (7) to describe the contact angle at a solid surface in the presence of air:[2.26]

$$\cos \theta' = f \cos \theta + (1-f) \cos 180^0 = f \cos \theta + f - 1 \quad \text{(eq.7)}$$

where $f$ is described as the fraction of a wetted solid surface area to actual area of the solid surface and air is assumed to be superhydrophobic with a water contact angle of 180°.
2.5.2 Superhydrophobicity: Self-Cleaning Surfaces (Lotus Effect)

Superhydrophobicity can be observed in nature. For example, lotus leaf shows a superhydrophobic surface.\textsuperscript{[2.27,2.28]} The water drops on the lotus leaf bead up with a contact angle of about 160°. When rain falls on the leaf, water drops roll off and collect some dirt along the way. Thus, superhydrophobic surfaces possess a “self-cleaning” ability. This behavior is called “Lotus effect”.\textsuperscript{[29,30]} Why do nature plants, e.g., “lotus leaf” or “rice leaf”, etc., present superhydrophobic properties on the surfaces? There are two reasons to explain “Lotus effect”. Under the careful examination of SEM, the leaves
of the natural plants with Superhydrophobicity (e.g. rice leaf, lotus leaf, etc.) show very rough surfaces with micro- and nano-scale hierarchical structures resulting from the microstructures covered with nanostructures (hair-like nanofibers).\textsuperscript{[29,30]} In addition, there is also a thin layer of the epicuticular wax coated on the nanostructured surfaces.\textsuperscript{[2.29-2.31]}

Recently, the superhydrophobic surfaces have been obtained via the bio-mimic micro- and nanofabrication,\textsuperscript{[2.29-2.68]} i.e., making a very rough surface following by coating of a thin layer of materials of low surface free energy (e.g. fluorinated compounds, CF\textsubscript{4})\textsuperscript{[2.38-2.43]} or making a very rough surface directly from the hydrophobic materials.\textsuperscript{[2.46,2.52]}

\subsection*{2.5.3 Superhydrophilicity: Anti-Fog Surface}

In humid conditions, atmospheric moisture condenses as droplets on the surfaces of superhydrophobic, hydrophobic, or hydrophilic solid materials. The water beads built up on the windows result in the reduction of light transmitting, called fog. However, the water droplets will spread out instead of forming beads on the surfaces of superhydrophilic substrates. Therefore, the most popular application for superhydrophilic materials is anti-fog coating.\textsuperscript{[2.69-2.76]}

\subsection*{2.5.4 Smart Surfaces with Reversible Wettability: Electrowetting}

A surface with reversible switching between the superhydrophilicity and superhydrophobicity via external stimuli of environment at different conditions has
attracted much interest for the development of smart surfaces. In general, the superhydrophilicity and superhydrophobicity can be achieved through controlling the roughness on hydrophilic and hydrophobic surfaces, respectively. As mentioned above, two properties, i.e. chemical composition and surface roughness, determine the superhydrophilicity and superhydrophobicity. Thus, the reversible switching can be achieved via changing the surface chemical structures by external stimuli at the same topography. Stimuli-responsive surfaces show that the reversible wettability can be controlled by various stimulus methods including electrical field,\[^2,77\] thermal treatment,\[^2,78,2,79\] light irradiation,\[^2,51,2,53,2,80\] pH-values,\[^2,81,2,83\] biaxial extension and unloading,\[^2,82\] etc.

Reversible switching between the hydrophilicity and hydrophobicity is also an interesting processing for electronic, biological, and microfluidic applications in the industry. Recently, Hayes et al. used electrowetting (external force) to reversibly control the surface tension to manipulate the colored oil motion on the transparent electrode.\[^2,84\] They claimed that this technique can be used to fabricate reflective full-color electronic display and the device showed that the reflectivity and contrast are four times brighter than reflective liquid-crystal displays and twice as bright as devices made by other emerging fabrication. They concluded that electrowetting at low voltages was a promising technique to fabricate a wide range of electro-optic devices.
REFERENCES: CHAPTER 2


CHAPTER 3

EXPERIMENTAL

3.1 REAGENTS

Aniline (Aldrich) and pyrrole (Aldrich) were distilled under vacuum before use. Ammonium peroxydisulfate (APS; Aldrich), deionized water (OSU Chemical Reagent Store) and dopant acids were used directly as received without further purification. Spectra/Por Dialysis Tubing, Regenerated Cellulose (MWCO 3500, MWCO 12k-14k, MWCO 15K, MWCO 25K, and MWCO 60K), and Spectra/Por Closures were purchased from Spectrum Laboratories, Inc. A variety of inorganic/organic dopant acids were used to study the formation of polyaniline nanofibers in the dilute polymerization and porous membrane controlled polymerization, including hydrochloric acid (HCl), sulfuric acid (H₂SO₄), perchloric acid (HClO₄), phosphoric acid (H₃PO₄), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), p-toluenesulfonic acid (p-TSA), (1S)-(+)10-camphorsulfonic acid (CSA), methanesulfonic acid (CH₃SO₃H), nitric acid (HNO₃), etc. The surface coating of poly (ethylene terephthalate) over-head transparency (PET; University of Yamanashi, Collage Bookstore, Japan) was removed by gently wiping in one direction using fine tissue paper and acetone. The transparency treated by acetone is
labeled as “bare-PET” and untreated is labeled as “PET”. A glass coated with ITO and the substrates were cleaned by sonication in RBS solution (10 ml of concentrated RBS-38, 5 ml of ethanol and 485ml of Deionized water) for at least 30 minutes and then rinsed by plenty of deionized water before use.

3.2 DILUTE POLYMERIZATION

Preparation of polyaniline nanofibers: aniline was dissolved in a small portion of 1M dopant acid solution, and carefully transferred to the solution of ammonium peroxydisulfate (APS) dissolved in 1M dopant acid solution in the beaker as shown in Figure 3.1. The reaction was carried out at room temperature without any disturbance. After 24 hours, the dark-green precipitate was collected either using dialysis tubing (MWCO 12k-14k), and then purifying by dialysis against deionized water or using a Buchner funnel with a water aspirator and then purifying portionwise with deionized water until the filtrate became colorless. In the reaction mixture the initial concentration of aniline to the total volume of solution was maintained at 8mM, and the molar ratio of aniline to APS was kept at 2 for all syntheses reported here.
Figure 3.1: Images illustrating dilute polymerization.

3.3 POROUS MEMBRANE CONTROLLED POLYMERIZATION

As an illustrative case, we chose regenerated cellulose dialysis tubing with molecular weight cut-off (MWCO) 3,500 (Spectra/Por 3, Spectrum Laboratories, Inc.) as a permeable membrane, aniline as a monomer, ammonium persulfate as an oxidant and inorganic/organic acid as a dopant acid. Aniline was dissolved in 12mL of 1M dopant acid solution, and carefully transferred to dialysis tubing (MWCO 3500) sealed with Spectra/Por Closures. The sealed dialysis tubing was put into the 600mL beaker with the solution of ammonium peroxydisulfate dissolved in 500mL of 1M dopant acid solution. The reaction was carried out at room temperature or temperature 0-5 °C (ice bath)
without any disturbance or with stirring. The blue-green tint started to appear at the interface of the dialysis tubing after the induction time of the reaction as shown in Figure 3.2. After 24 hours, the precipitated dark-green polyaniline outside the dialysis tubing was collected and purified using the same procedures as mentioned in the dilute polymerization.

![Image](image_url)

Figure 3.2: Polyaniline nanofibers formed at the interface of the porous membrane.

### 3.4 FABRICATION OF ALIGNED AND ORIENTED NANOFIBERS

Two methods as mentioned above (dilute polymerization and porous membrane controlled polymerization) were used to fabricate aligned and oriented nanofibers of polyaniline and its derivatives. The solid substrates were immersed into or suspended in APS/1M dopant acid solution and then aniline (or monomer)/1M dopant acid solution
was added (or vice versa). The polymerization was carried out with stirring by a magnetic bar at temperature 0-5 °C (ice bath) for 24 hours. For comparison, the polymerization was also carried out without disturbance at temperature 0-5 °C (ice bath) for 24 hours. For comparison, the polymerization was also carried out with stirring by a magnetic bar or without disturbance at room temperature for 24 hours. The molar ratio of aniline to APS was varied from 1 to 4.35.

3.5 MOLECULARLY FUNCTIONALIZED POLYANILINE NANOFIBERS

Polyaniline nanofibers and aligned polyaniline nanofibers were molecularly functionalized by nucleophilic addition using nucleophile (e.g. sulfite). The suspension of the nanofibers or the large arrays of the aligned nanofibers coated on a variety of substrates of various sizes were suspended in the aqueous solution of 0.1M of sodium metabisulfite or sodium bisulfite or sodium sulfite for the desired time at room temperature. The modified samples were purified or rinsed several times by a copious of deionized water.

3.6 DOPING, DEDOPING AND REDOPING

Doped polyaniline nanofibers or samples prepared here were dedoped by 0.1 M NH₄OH (aq), and then redoped by 0.5M or 1M HCl (aq). It is noted that the acids as
mentioned above can also be used to dope or redope nanofibers and many of basic solutions (e.g. NH₄OH\textsubscript{(aq)}, NaOH\textsubscript{(aq)}, etc.) can also be used to dedope nanofibers.

### 3.7 CHARACTERIZATION

Samples deposited onto the Si-wafer substrates and then sputtered with a thin layer of Au/Pd or Au were used for scanning electron microscopy (SEM, Philips XL-30 ESEM) studies. Samples dispersed in deionized water were transferred to copper grids for transmission electron microscopy (TEM, Philips CM-200 or Philips TF-20). UV/vis absorption was studied using a UV/VIS/NIR Spectrometer (PERKIN ELMER Lambda 19) employing the polyaniline dispersions in deionized water. Samples dispersed in deionized water were transferred to Rigaku glass powder holder for the study of X-ray diffraction. X-ray patterns were taken with CuK\(\alpha\) radiation (\(\lambda = 1.54059292\) Å). The electrical characteristics of the samples as prepared were performed by Keithley 487 PICOAMMETER/VOLTAGE SOURCE in the atmosphere at room temperature. The thicknesses of the films were determined by Surface Profiler (Tencor Instruments, Alpha-Step 500).
REFERENCES: CHAPTER 3


CHAPTER 4

RESULTS AND DISCUSSION

4.1 DILUTE POLYMERIZATION

Typical TEM and SEM images obtained demonstrate the nanofibrous structures of polyaniline as shown in Figure 4.1 and Figure 4.2, respectively. As long as polymerizations are performed using dilute aniline, nanofibers are formed regardless of which acids are used, such as those mentioned in the experimental section. Polyaniline nanofibers produced with different acids show similar nanofiber structures of interconnected networks. However, different types of acids can produce polyaniline nanofibers with different diameters. As shown in Figure 4.1(a), polyaniline nanofibers obtained from CSA\textsubscript{(aq)} present smaller diameters of 17 - 50nm. The diameters of polyaniline nanofibers synthesized in CH\textsubscript{3}SO\textsubscript{3}H\textsubscript{(aq)} range from 42nm to 70nm as shown in Figure 4.1(b). In addition, Figure 4.1(c) shows larger diameters of polyaniline nanofibers obtained from HClO\textsubscript{4}(aq) varying from 72nm to 250nm. The diameters of nanofibers described here are based on multiple statistical TEM measurements on different areas. Nanofiber morphology for each of the acids used is reproducible for the same synthesis conditions, such as concentration, temperature, etc. This indicates that the
The morphology of doped nanofibers does not significant change when dedoped and redoped multiple times by 0.1M NH\textsubscript{4}OH\textsubscript{(aq)} and 1M dopant acids, respectively. However, the nanofibrous structures are deformed or broken into fragments of small pieces under high-pressure mechanical stress, e.g. 2500 KPa, or an intense ultrasonic bath. Polyaniline nanofibers obtained in dilute aniline are easily dispersed in deionized water, methanol, ethanol or toluene etc., and the resulting suspensions are stable for several minutes, followed by agglomeration and precipitation. The suspension increases the processibility of polyaniline nanofibers. For example, we use the suspension of nanofibers to cast a thick film, \(\sim 10\mu\text{m}\), on a substrate and then immerse it into electrolyte solutions or solvents. Surprisingly, the thick film is stable in the solutions or solvents for more than one day without any dissolution. This may reflect the strong interaction and the highly entangled aggregation among the nanofiber networks as shown in SEM images (Fig. 4.2).
Figure 4.1: Transmission electron micrograph (TEM) of polyaniline nanofibers obtained in different dopant acids (a) CSA (b) CH₃SO₃H (c) HClO₄ and the inset image shows different area with nanofibers of larger diameters.

Figure 4.2: Scanning electron micrograph (SEM) of polyaniline nanofibers obtained from different dopant acids (a) CSA (b) CH₃SO₃H (c) HClO₄.
Figure 4.3: Scanning electron micrograph (SEM) of polyaniline nanofibers obtained in 1M HCl$_{aq}$ (a)-(b) conventional polymerization: [aniline] = 0.4M$^{[4.2]}$, (c)-(d) dilute polymerization: [aniline] = 0.008M. The white spots in the dashed circle in (d) may correspond to surface active sites for nucleation.

The formation mechanism of polyaniline nanofibers remains unclear. We suggest that the growth of nanofibers is intrinsic to the polymerization of aniline because it is observed even during synthesis with a relatively high concentration of aniline (SEM image, Figs. 4.3(a)-4.3(b)). However, in contrast to polymerization in a dilute solution (Figs. 4.3(c)-4.3(d)), for polymerization in concentrated solution the individual polyaniline nanofibers pack very densely and merge with each other as shown in Figure 4.3(b). According to classical nucleation theory,$^{[4.3,4.4]}$ nanofibers formed initially may serve as nucleation sites for additional nanofibers (secondary nucleation$^{[4.4]}$). We observe
small white spots on the nanofiber surfaces, e.g. Figure 4.3(d) within the dashed circle, which are associated with asperities along the fibers. We suggest that these may act as surface active sites for nucleation.\textsuperscript{[4.5-4.8]}

The formation of the interconnected, branched nanofiber networks may be explained as follows: In the event of high aniline concentration in solution, a competition between directional fiber growth process and formation of additional nucleation centers is taking place. Once a high density of nucleation centers is generated, the interfacial energy between the reaction solution and nanofibers may be minimized\textsuperscript{[4.3,4.6-4.8]} and hence rapid precipitation occurs, in a disordered manner, yielding irregular shapes. In a dilute solution the number of nucleation sites formed on the surface of the nanofibers may be reduced, thus allowing polyaniline to grow only in a one-dimensional morphology.

Polyaniline/HClO\textsubscript{4} nanofibers are dispersed in deionized water via vigorously shaking by hand for UV/vis absorption studies. Figure 4.4 shows UV/vis absorption spectra of polyaniline nanofibers obtained from HClO\textsubscript{4}(aq). After purification by dialysis against deionized water, polyaniline nanofibers present three absorption peaks c.a. 338nm, 430nm and 960nm (free carrier tail)\textsuperscript{[4.9,4.10]} as shown in the dotted line of Figure 4.4. By adding one drop of dilute 70% w/w HClO\textsubscript{4}(aq) to the above polyaniline nanofiber dispersion (dotted line), the absorption intensity of the peaks at c.a. 338nm decreases, simultaneous with the increase of the absorption intensity of the peak at c.a. 430nm and 960nm (free carrier tail) as shown in the dashed line of Figure 4.4. It is possible that the purification of polyaniline nanofibers by dialysis with deionized water results in removal of the dopant, HClO\textsubscript{4}, within polyaniline backbone to form partially doped polyaniline
nanofibers. Furthermore, adding a drop of 30% w/w NH₄OH (aq) to polyaniline/HClO₄ nanofibers dispersion (dashed line) introduces the formation of an absorption band c.a. 677nm, simultaneously resulting in disappearance of two absorption bands c.a. 430nm and 960nm (free carrier tail) as shown in the solid line of Figure 4.4. The two strong absorption bands c.a. 338nm and 677nm are attributed to the formation of emeraldine base.\textsuperscript{[4.11-4.15]} The UV/vis absorption patterns of polyaniline nanofibers obtained are consistent with previously reported results.\textsuperscript{[4.9,4.10,4.16-4.19]}

Figure 4.4: UV/vis spectra of polyaniline/HClO₄ nanofibers dispersed in deionized water after purification (dotted line, ….), after adding a drop of dilute HClO₄ (aq) (dashed line, -- --) and after adding a drop of 30% w/w NH₄OH (aq) (solid line, — ).
Figure 4.5 shows X-ray diffraction (XRD) pattern of doped polyaniline nanofibers obtained from \( \text{HClO}_4(\text{aq}) \). Two intense broad bands centered at \( 2\theta \sim 20^\circ \) and \( \sim 25^\circ \) show that these nanofibers are partially crystalline. Comparing to previously reported data,\(^{[4.20-4.22]}\) there are no significant differences between the structural order of polyaniline nanofibers and that of nonfibrous polyaniline powders or films.

![X-ray diffraction pattern](image)

**Figure 4.5:** X-ray diffraction pattern of the film formed by casting doped polyaniline/\( \text{HClO}_4 \) nanofibers from deionized water dispersion.
The suspension of polyaniline nanofibers obtained from HClO₄(aq) was deposited and dried to form a dark green film on a glass slide prepatterned with four Au electrodes constructed by thermal evaporation. The bulk room temperature DC conductivities of polyaniline/HClO₄ nanofibrous film are in the range of 2 - 4 S/cm obtained from the standard 4-probe method. Based on UV/vis studies as shown in Figure 4, we suggest that an individual nanofiber has a higher R.T. DC conductivity than nanofibrous films. This is supported by the free carrier tail associated with delocalization of electrons in the “polaron” band as demonstrated by Ref. [4.9, 4.10, 4.17]. As the inter-fiber interaction is negligible in these very dilute suspensions, the characteristics of the spectra are related to the properties of the individual nanofibers only. Furthermore, as shown earlier,[4.23,4.24] there also is significant inter-fiber contact resistance between the individual nanofibers produced by using surfactants,[4.25,4.26] thereby decreasing of the bulk conductivity.

In summary, polyaniline nanofibers are successfully synthesized for the first time using dilute polymerization resulting in the careful control of nucleation and growth. This is accomplished via reducing the concentrations of both monomer and oxidant with a constant molar ratio. We also demonstrate that different dopant acids produce similar morphology of polyaniline nanofibers. Additionally, the diameters of polyaniline nanofibers are tunable under the appropriate selection of dopant acids. The dispersion of polyaniline nanofibers can be cast to form highly porous nanofibrous films without deformation of the nanofiber morphology. UV/vis absorption and X-ray diffraction structure show that polyaniline nanofibers have similar absorption and diffraction patterns to those previously reported for nonfibrous polyaniline.[4.1,4.20-4.22,4.27-4.30] This
also supports that the nanofibrous polyaniline has very similar chemical structure to granular polyaniline.

### 4.2 POROUS MEMBRANE CONTROLLED POLYMERIZATION

Figure 4.6 shows the polymerization procedures. Aniline monomer dissolved in an aqueous acid solution is separated by a permeable membrane from an aqueous oxidant/acid solution in a reaction chamber (Fig. 4.6(a)). Aniline monomer (or oxidant) diffuses through the membrane at a controlled rate and is subsequently polymerized in the oxidant/acid solution (or aniline solution) according to known reactions.\[^{[4.2,4.31]}\]

Alternately or in addition to diffusion of aniline monomer, the oxidant can diffuse through the membrane. Once polymerization occurs, polyaniline nanofibers form at the membrane/solution interfaces and then precipitate out of aniline or oxidant solution (Fig. 4.6(b)). Simultaneously, the pores of the membrane shrink in diameters and then are blocked due to the precipitation of polyaniline resulting in the termination of the polymerization (Fig. 4.6(f)). This phenomenon can be described as a porous membrane controlled polymerization. When the polymerization is completed, polyaniline nanofibers are collected directly outside or inside the tubing without any further treatment (Fig. 4.6(f)), unlike template synthesis\[^{[4.32,4.33]}\] which requires the removal of the templates to obtain free-standing nanofibers.
Figure 4.6: Images illustrating porous membrane controlled polymerization. Polymerization conditions: Spectra/Por Dialysis Tubing (MWCO: 12k-14k; flat width: 25mm), [aniline]=1.61mmoles / 5ml of 1.2M HCl (inside the tubing), and [APS]=0.8mmoles / 200ml of 1.2M HCl (outside the tubing), temperature = room temperature. The images were captured at time=(a) 0min, (b) 15min, (c) 23min, (d) 26min, (e) 1hour 27min, (f) 24hours. The orange color bars on images are Spectra/Por Closures used to seal the tubing.

A variety of inorganic/organic dopant acids were used to study the formation of polyaniline nanofibers in the porous membrane controlled polymerization, including inorganic acids (e.g. hydrochloric acid (HCl), sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), perchloric acid (HClO₄), etc.), and organic acids (e.g. 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), p-toluenesulfonic acid (p-TSA), (1S)-(+)10-camphorsulfonic acid (CSA), methanesulfonic acid (CH₃SO₃H), etc.). All precipitates show very similar nanostructured morphology. In addition, regardless of molar ratio of
aniline to APS used (e.g. ranging from 4/1 to 1/2) and the concentration of dopant acids used (e.g. 0.2M to 6M) polyaniline precipitates obtained all present nanofibrous structures. However, the average diameters of nanofibers are dependent on polymerization temperature. For example, nanofibers synthesized in HClO$_4$ (aq) at room temperature show larger diameters ranging from 70nm to 180nm (average diameter ~ 130 nm) confirmed via TEM than those obtained at lower temperature, 0~5 °C (ranging from 50nm to 100nm; average diameter ~ 80 nm). It is obvious that temperature controls the releasing rate of the reagents through the porous membrane and also affects the formation sizes of the nuclei of polyaniline.

We choose perchloric acid as an illustrative case. The purified dark green precipitate was dispersed in deionized water or ethanol and a thin film was cast onto silicon wafer for examination by scanning electron microscopy (SEM, Philips XL-30 ESEM) and onto a copper grid for transmission electron microscopy (TEM, Philips CM-200 or Philips Tecnai F20). As shown in Figure 4.7 (SEM and TEM images), the dark green precipitate is comprised of nanofibrous structures with diameters ranging from 50nm to 100nm (average diameter ~ 80 nm), confirmed via TEM. The uniformity of polyaniline nanofibers obtained can be observed from the SEM image of Figure 4.7(a) at low magnification (×100), with a scale bar = 200μm. It shows nearly ~100% of nanofibers formed in this chemical polymerization with the porous membrane control, which is demonstrated by a high magnification SEM image (×20,000) of Figure 4.7(b). Figure 4.7 also show that polyaniline nanofibers are of the interconnected, branched and networked morphology. However, after dilution of the colloid suspension of polyaniline
nanofibers with large amounts of water or ethanol, some single polyaniline nanofibers can be isolated from the agglomeration (Fig. 4.7(c)). It indicates that this kind of polyaniline nanofibers can be potentially used to fabricate nanoelectronic devices such as field-effect devices,\textsuperscript{[4.34-4.36]} which are under investigation. Polyaniline nanofibers formed within the dialysis tubing also show very similar nanostructures as those found outside. There are also no significant differences on the nanostructured morphology as nanofibers are dedoped and redoped multiple times by base and acid solutions, respectively.
Figure 4.7: (a, b and c) Scanning electron micrograph (SEM) of polyaniline nanofibers prepared by porous membrane controlled polymerization. Samples are deposited on Si-wafer substrate with a thin layer coating of Au/Pd. (a) Low magnification, x100; scale bar=200μm (b) High magnification, x20,000; scale bar=1μm (c) Isolated single nanofibers; magnification, x10,000; scale bar=2μm. (d and e) Transmission electron micrograph (TEM) of polyaniline nanofibers dispersed in ethanol under ultrasonic bath, and then deposited on copper grid substrate. (Scale bar = (d) 200nm (e) 50nm). Polymerization conditions: Spectra/Por 3 Dialysis Tubing (MWCO: 3,500; Flat width=45mm) [aniline] = 4.025mmoles/12ml of 1MHClO₄(aq) (inside the tubing), [APS] = 4.025mmoles/500ml of 1MHClO₄(aq) (outside the tubing), temperature = 0~5 °C (ice bath), reaction time = 24h and without disturbance.
Figure 4.8 shows XRD patterns of polyaniline nanofibers obtained. After purification by deionized water, as-prepared polyaniline nanofibers which is in-situ doped by HClO₄ are dispersed in 0.1M HClO₄(aq), termed ES-ClO₄. The XRD pattern of ES-ClO₄ reflects a partially crystalline structure (Fig. 4.8(a)). According to our previous results,[4,21,4,22] ES-ClO₄ belongs to class I (ES-I) and is typical for partially protonation with HClO₄(aq). One intense broad band centered at 2θ ~ 20°, a shoulder at 2θ ~ 30°, and a weak band at 2θ ~ 45° show that emeraldine base form (EB) of polyaniline nanofibers obtained is a strongly disordered polymer (Fig. 4.8(b)) which agrees with the electron diffraction pattern obtained (not shown). This diffraction pattern is in agreement with that of non-fibrous emeraldine base samples, EB-I.[4,21,4,22] When nanofibrous EB is redoped by HCl(ν) vapor (labeled as ES-Cl-vapor) or aqueous 0.5M HCl(aq) (labeled as ES-Cl-p), respectively, new crystalline structures are introduced (Figs. 4.8(c)-4.8(d)). Comparing to our earlier publications,[4,21,4,22] the XRD patterns of ES-Cl-vapor and ES-Cl-p are ascribed to class I material (ES-I) by the preparation procedures, and generally possess ES-I crystal structures. Similarly, the X-ray diffraction patterns of ES-Cl-vapor (Fig. 4.8(c)) and ES-Cl-p (Fig. 4.8(d)) are similar to that of ES-I as expected.[4,21,4,22]
Figure 4.8: X-ray diffraction (XRD) patterns of polyaniline nanofibers. After purification, as-prepared polyaniline nanofibers are only partially doped by HClO$_4$(aq). The sample is equilibrated with 0.1M HClO$_4$(aq) (labeled as ES-ClO$_4$) (a). After purification (and without treatment by 0.1M HClO$_4$(aq)), the as-prepared sample is dedoped by 0.1M NH$_4$OH(aq), and then washed by deionized water to form emeraldine base (EB) (b). After XRD measurement of the sample b, it is exposed to HCl$_{(v)}$ vapor for 30 minutes (labeled as ES-Cl-vapor) (c). A second portion of sample b (undoped polyaniline nanofibers, EB) is redoped by 0.5M HCl(aq) and then washed by dialysis against deionized water (labeled as ES-Cl-p) (d). All dispersed samples are deposited on Rigaku glass powder holder for measurement. X-ray patterns were taken with CuKα radiation (\(\lambda=1.54059292\) Å). Polymerization conditions: Spectra/Por 3 Dialysis Tubing (MWCO: 3,500; Flat width=45mm), [aniline] = 4.025mmoles/12ml of 1MHClO$_4$(aq) (inside the tubing), [APS] = 4.025mmoles/500ml of 1MHClO$_4$(aq) (outside the tubing), temperature = 0–5 °C (ice bath), reaction time = 24h and without disturbance.
UV/vis absorption spectra (Fig. 4.9) demonstrate that polyaniline nanofibers obtained have different absorption patterns corresponding to different protonation levels and are in excellent agreement with the UV/vis absorption spectra of nonfibrous polyaniline powders of the similar doping level.\textsuperscript{[4.16-4.19]} This supports the presence of the same chemical structure for nanofibrous polyaniline and granular (nonfibrous) polyaniline. Furthermore, we note that based on UV/vis absorption (Figs. 4.9(b)-4.9(d)), ES-Cl-p shows partial protonation with HCl.
Figure 4.9: UV/vis spectra of polyaniline nanofibers. (a) Emeraldine base form (EB) of polyaniline nanofibers (blue solid line, \( \cdots \)). We note that the unusually broad nature of the peak at 500-900 nm suggests greater planarity of the polymer chains and/or the possible presence of residual dopants in these nanofibers. (b) Undoped polyaniline nanofibers (EB) was redoped by 0.5M HCl\(_{(aq)}\), and then washed by deionized water to form the dispersion of the partially doped emeraldine salt, termed ES-Cl-p (brown dotted line, \( \cdots \)). (c) ES-Cl-p precipitate was redispersed in a large amount of deionized water for UV/vis study, resulting in the partial removal of counter ion within the polymer backbone to form ES-Cl-w (red dash dotted line, \( \cdots \cdots \)). (d) Addition of a droplet of aqueous 37% w/w HCl\(_{(aq)}\) to the above dispersion, ES-Cl-w (red dash dotted line) results in fully doped polyaniline nanofibers, ES-Cl (green dashed line, \( \cdots \cdots \)).

Polymerization conditions: Spectra/Por 3 Dialysis Tubing (MWCO: 3,500; Flat width=45mm) [aniline] = 4.025mmoles/12ml of 1MHClO\(_4\)\(_{(aq)}\) (inside the tubing), [APS] = 4.025mmoles/500ml of 1MHClO\(_4\)\(_{(aq)}\) (outside the tubing), temperature = 0–5 °C (ice bath), reaction time = 24h and without disturbance.
The dispersion of polyaniline nanofibers was deposited onto a glass slide to form a dark porous green film. Subsequently, four Au electrodes were deposited by thermal evaporation to form the contacts. The bulk conductivity for the redoped nanofiber (ES-Cl-p) array is obtained in the range of 0.9-1.3 S/cm based on the standard 4-probe DC measurement at room temperature. As the sample ES-Cl-p is exposed to HCl(V) vapor, the conductivity is changed to 2.3-2.5 S/cm. This reconfirms that ES-Cl-p is partially doped by HCl as mentioned above. The bulk R.T. DC conductivity of the nanofiber film is comparable to that of the nonfibrous powder. However, we suggest that an individual nanofiber has a higher conductivity than those films because the free carrier tails associated with delocalization of electrons in the “polaron” band are shown in UV/vis absorption spectra of doped polyaniline nanofibers (Fig. 4.9). As very dilute dispersion of nanofibers is used in the optical study, the characteristic of UV/vis absorption is only related to the properties of individual nanofibers. Thus, the lower bulk R.T. DC conductivity of the nanofiber film is attributed to the existence of the inter-fiber contact resistant.

For increased control of the nanofiber preparation, we used two segments of dialysis tubing to separate aniline and oxidant, respectively. The product also shows extremely similar nanofibrous morphology to those obtained from one dialysis tubing used. When the solvent inside dialysis tubing is replaced with organic solvents (e.g. toluene), there is no obvious difference observed for the nanofibrous morphology. The nanofibers are also formed exclusively when the reaction is carried out with disturbance (e.g. stirring); however, the majority of the products are precipitated inside the tubing.
We also produce nanofibers of many of the derivatives of polyaniline by porous membrane controlled polymerization (e.g., nanofibers of “self-doped” sulfonated polyaniline (Fig. 4.10) and poly (o-toluidine) (Fig. 4.11)), thereby allowing preparation of nanofibers of a wide variety of polyaniline nanofibers and also control of the chemical, processing and electrical properties. These nanofibers will have broad applicability in areas ranging from cell culture, to electronic devices, to sensors, to supercapacitors, as well as many others.

Hence, the approach described here provides a significant possibility to synthesize conductive/semiconductive polymer and copolymer nanofibers. We note that it may also be widely applicable to the fabrication of the nanofibers of non-conductive polymers.

In summary, high-quality polyaniline nanofibers are successfully synthesized for the first time using porous membrane to control the polymerization of polyaniline resulting in the careful control of nucleation and growth in the initial stage of the polymerization. The diameters of polyaniline nanofibers are tunable under the appropriate selection of dopant acids and/or temperature. The dispersion of polyaniline nanofibers can be cast to form highly porous nanofibrous films without deformation of the nanofiber morphology. UV/vis absorption and X-ray diffraction structure show that polyaniline nanofibers have similar absorption and diffraction patterns to those previously reported for nonfibrous polyaniline. This also supports that the nanofibrous polyaniline has very similar chemical structure to granular polyaniline.\[4.1,4.20-4.22,4.27-4.30\]
Figure 4.10: Scanning electron micrograph (SEM) of sulfonated polyaniline nanofibers prepared by porous membrane controlled polymerization. Polymerization conditions: Spectra/Por Dialysis Tubing (MWCO: 12k-14k; Flat width=25mm), [aniline] = 1.61mmoles/5ml of 1.0M HCl (inside the tubing), [metanilic acid] = 32.2mmoles and [APS] = 0.8mmoles/200ml of 1.0M HCl (outside the tubing), temperature = room temperature, reaction time = 24h and without disturbance. (a) Low magnification; scale bar=1mm. (b) High magnification; scale bar=1μm.

Figure 4.11: Scanning electron micrograph (SEM) of poly (o-toluidine) nanofibers prepared by porous membrane controlled polymerization. Polymerization conditions: Spectra/Por Dialysis Tubing (MWCO: 12k-14k; Flat width=25mm), [CSA] = 0.2M, [o-toluidine] = 1.87mmoles/5ml of 0.2M CSA (inside the tubing) and [APS] = 0.8mmoles/200ml of 0.2M CSA (outside the tubing), Temperature = room temperature, reaction time = 24h and without disturbance.
4.3 ALIGNED AND ORIENTED NANOFIBERS OF POLYANILINE AND ITS DERIVATIVES

The highly uniform, green and transparent thin films deposited by dilute polymerization or porous membrane controlled polymerization are very strongly adhered onto the substrates. The morphology of the thin film is examined by SEM. As shown in Figure 4.12, the thin film deposited by dilute polymerization shows morphology with aligned and well-oriented polyaniline nanofibers. The thin film shows very uniform white-bright spots when the film is observed from the top (Figs. 4.12(a)-4.12(b)). Those white spots actually are the tips of nanofibers (Fig. 4.12(c)). When the sample is tilted at a certain angle (e.g. 50°), those nanofibers appear (Figs. 4.12(d)-4.12(f)). A close view to the edge of thin film partly removed by Scotch tape shows that those nanofibers are perpendicular to the substrates (Fig. 4.12(f)). The diameters of the tips of the single nanofibers range from 20nm to 40nm. Some nanofibers tend to merge together to form a bundle resulting in a larger white spot with diameters ranging from 40nm to 70nm. The average length of the uniform aligned nanofibers is ~360nm, confirmed by Surface Profiler (Tencor Instruments, Alpha-Step 500).

The morphology of the aligned and oriented nanofibers is sensitive to the temperature and concentration of the reagents used for polymerization. For example, low temperature promotes the formation of aligned and oriented nanofibers (Fig. 4.12). When the reaction is carried out at room temperature (e.g. ~24 °C), the morphology of the thin film deposited is extremely similar to that of the nanofibers obtained in bulk solution (Figure 4.13).
Figure 4.12: Scanning electron micrograph (SEM) of aligned polyaniline nanofibers grown on the overhead transparency (bare-PET). (a) Top view, low magnification. (b)-(c) Top view, high magnification. (d)-(e) Tilted view, high magnification. (f) Tilted view for the edge of the partially removed thin film. Polymerization conditions: [aniline] = 0.01M, [aniline]/[APS] = 1.5, Temperature = 0–5 °C (ice bath), stirring reaction, and [HClO₄] = 1M.

Figure 4.13: Scanning electron micrograph (SEM) of polyaniline nanofibers grown on the microscope glass slide. The upper notation is the polymerization temperature.
When the initial concentration of aniline is used in the range of 8mM to 12mM and reaction is performed at low temperature (e.g. 0~5 °C), all thin films deposited show similar morphology with aligned and oriented nanofibers (Fig. 4.14(c)-4.14(e)). There is no apparent difference on the morphology of aligned and oriented polyaniline nanofibers when the sizes of the reaction chambers or containers (reaction volume) are reduced or enlarged several times as long as the initial concentration of the reagents is fixed in the range of 8mM to 12mM. All morphology of aligned and oriented polyaniline nanofibers for the same polymerization conditions is reproducible. This indicates that the methods we propose here allow us to scale up the coating of aligned and oriented nanofibers on the substrates. For example, we have successfully deposited the aligned and oriented nanofibers onto a wide variety of substrates of various sizes and geometries, including poly (ethylene terephthalate) (PET) submicrofibers, the microchannels of any size and micropillars of any size, 8.5 inches x 11 inches letter sized transparency, glasses or glasses coated by ITO of various sizes, etc. The same morphology is also observed on molecularly modified substrates (e.g. 3-aminopropyltriethoxysilane (APTES)-modified glass). The free-standing thin film collected at the interface of air and reaction solution also shows the same morphology as those found on the substrates. Mixing conditions (stirring or no stirring) and choice of dopant acids only slightly affect on the final morphology. However, uniformity of the coating is improved when the monomer and oxidant are distributed homogenously during the polymerization.
Figure 4.14: Tilt-viewed scanning electron micrograph (SEM) of aligned polyaniline nanofibers grown on the over-head transparency (PET). The left-upper notation is the initial concentration of aniline used for polymerization, where mM = 10^{-3} M. The molar ratio of aniline to APS was fixed at 1.5. All polymerization was carried out and in the ice bath (0~5 °C) and [HClO₄] = 1M.

Aligned and oriented polyaniline nanofibers were deposited onto over-head transparency (bare-PET) for UV/vis absorption studies. Figure 4.15 shows UV/vis absorption spectra of the thin film of polyaniline obtained from HClO₄(aq). Two absorption bands c.a. 430nm and 860nm (free carrier tail)\cite{4,9,4,10} were observed for the different initial concentration of aniline used for polymerization. UV/vis absorption
patterns of the thin films of aligned and oriented polyaniline nanofibers as deposited are consistent with previously reported results. As shown in Figure 4.15, the absorption intensities at 400nm vary from the initial concentration of aniline used for polymerization. The maximum intensity of UV/vis absorption at 400nm is observed when 10mM (0.01M) of the initial concentration of aniline is used (Figs. 4.15-4.16). The thickness of the thin film is also found to be varied by the initial concentration of aniline used. For example, the measured thickness of the thin film is ~360nm for 10mM of aniline and ~300nm for 12mM of aniline. Thus, the maximum intensity of UV/vis absorption at 400nm may be associated to thickest thin film.

![Figure 4.15: UV/vis spectra of thin films of aligned and oriented polyaniline nanofibers grown on the over-head transparency (bare-PET). The notations on the spectra are the initial concentration of aniline used for polymerization, where mM = 10^{-3} M. Polymerization conditions: [aniline] = shown on the spectra, [aniline]/[APS] = 1.5, Temperature = 0~5 °C (ice bath), stirring reaction, and [HClO_4] = 1M.](image-url)
Figure 4.16: The intensities of UV/vis absorption at 400nm taken from the thin films of aligned and oriented polyaniline nanofibers grown on the over-head transparency. Polymerization conditions: [aniline] = shown on the spectra, [aniline]/[APS] = 1.5, Temperature = 0~5 °C (ice bath), stirring reaction, and [HClO₄] = 1M (where mM = 10⁻³ M).

4.4 FORMATION MECHANISM OF NANOSTRUCTURES

4.4.1 1-D Nanostructures: Anisotropic Growth, Secondary Nucleation and Growth

According to the classical theory of nucleation and growth,[4,3,4,4] the mechanism of nucleation followed by growth controls polyaniline morphology. Elongated form (e.g., fibers or rods) is established as the growth rate for polyaniline is distinctly not identical in
all directions (anisotropic growth). Moreover, new active nucleation centers could be formed on initially formed nanofibrils for additional growth of nanofibrils resulting in a branched network or dendrites (secondary nucleation\textsuperscript{[4,4]}).

4.4.2 Dilute Polymerization

In general, monomers and oxidants in the vicinity of initially formed nanofibrils are depleted in the early stage. In dilute polymerization, new reactive aniline cation-radicals and oligomeric intermediates generally do not diffuse quickly enough to those nanofibrils resulting in nanofibrillar surfaces surrounded by “depleted solution” (termed depleted region)\textsuperscript{[4,4]}. However, those nanofibrils are able to continuously grow and elongate in one direction because their ends extend to the “less depleted regions”\textsuperscript{[4,4]} as shown in Figure 4.17. Further, in dilute polymerization, a larger amount of polyaniline is able to be continuously deposited onto the active nuclei resulting in nanofibers with larger average diameters. This contrasts to the concentrated polymerization in which a large number of nanofibrils “suddenly” form and precipitate, then simultaneously followed by secondary nucleation and growth.\textsuperscript{[4,4]} Hence, the average sizes of nanofibers decrease. Likewise, polyaniline begins to grow into highly branched morphology, and then eventually develops into irregular shapes. Clearly, the more dilute the monomer/oxidant concentration, the less branched and the longer the nanofibers, and the larger the average diameters of nanofibers.

We noted that the anisotropy of the growth rate for some inorganic single crystals (e.g., CaSO\textsubscript{4}·2H\textsubscript{2}O) similarly depends on the solution concentration of components.\textsuperscript{[4,3,4,4]}
The increased sensitivity to stirring of fiber diameters and lengths for dilute solutions as compared to stirring effects for concentrated solution supports this model of secondary nucleation and the role of depleted regions. We also note that the formation of smaller diameter fibers at lower temperature (e.g., 0°C as compared to 24°C synthesis) may reflect thermally activated diffusion kinetics controlling the size of the “depleted region” surrounding each fiber.

Figure 4.17: Schematic representation of the growth and elongation of an initially formed nanofiber.
4.4.3 Porous Membrane Controlled Polymerization

In porous membrane controlled polymerization, the nuclei are initially formed at the interface of the membrane where more concentrated aniline (or oxidant) occurs. This results in the formation of initial formed nanofibers at the interface. The initial formed nanofibers tend to precipitate toward the bottom of the beaker resulting in the isolation of nanofibers from new reactive aniline cation-radicals and oligomeric intermediates. This also prevents initial formed nanofibers from the secondary nucleation and growth. The formation mechanism is similar to interfacial polymerization$^{[4,12,4,39]}$ or rapid-mixing reaction.$^{[4,27,4,39]$

4.4.4 Dopant Acid Effect

The different diameters of as-synthesized polyaniline nanofibers are resulted from the dopant acids using for protonic acid in the polymerization. To explain the dopant acid effect, we may have to understand the mechanism of polymerization of aniline first.

In oxidative chemical polymerization, aniline molecules are polymerized directly in an oxidant solution (e.g. ammonium persulfate) in the presence of protonic acid.$^{[4,2,4,14,4,40,4,41]}$ Figure 4.18 shows the proposed mechanism of chemical oxidative polymerization of aniline.$^{[4,41]}$ In the first step, aniline is oxidized to form anilinium cation-radical. This step is rate-determining. Two anilinium cation-radical are possible to form head-to-head, head-to-tail, and tail-to-tail type linkages. In the presence of the strong acids (pH $\leq 0$), head-to-tail type linkage is in favor of the formation of $N$-phenyl-1,4-phenylenediamine (aniline dimmer).$^{[4,41]}$ $N$-phenyl-1,4-phenylenediamine is oxidized
again to form cation-radical and then reacts with anilinium cation-radical to form trimer. The chain propagates continuously until it terminates when the certain molecular weight is achieved. This results in the formation of polyaniline.

From the proposed mechanism of polymerization of aniline, we know that anilinium cation-radicals are formed in the first step of polymerization. The formation of cations (positive charges) of aniline, dimmer, trimer,....,oligomers, etc, as well as emeraldine salt (posses positive charges in the polymer chains) is strongly correlated to anions (the negative charges). Most protonic acids provide anions (A⁻) in the solution. Anions tend to form ionic bonding (electrostatic force) with cations.⁴,⁴² Therefore, the aggregation of polymer chains is determined by the electrostatic force, intramolecular forces, and intermolecular forces (e.g. ionic bond, H-bond as well as the van der Waals interactions). The degree of aggregation of polymer chains formed determines the size of nuclei which plays an important role for further growth of nanofibers as mention above. Thus, we can only explain that different dopants will generate different strength of electrostatic force, H-bond, and van der Waals in the polymerization media, which directly affect the aggregation of oligomeric intermediates or polymer chains resulting in the different sizes of the stable nuclei; hence, producing fibers with different diameters. This is also confirmed by the solvent effect on polyaniline nanofibers.⁴,²⁷
4.4.5 Aligned and Oriented Polyaniline Nanofibers

The formation mechanism of aligned and oriented polyaniline nanofibers is very similar to the model proposed by Liu et al. There are two possible nucleation sites, i.e. bulk solution and solid substrates, for the growth of polyaniline in the oxidative chemical polymerization. These two sites are competitive to each other. It is known that the induction time is strongly dependent on the concentration of reagents (i.e. aniline, oxidant, and acids) in the polymerization of aniline. Concentrated aniline (or
oxidant) induces polyaniline to form in the bulk solution at a competitive or faster rate comparing to that in the solid substrates. However, when very dilute aniline (or oxidant) is used, most heterogeneous nucleation first occurs favorably on the foreign solid substrates. Consequently, most active nucleation centers are generated on the solid substrates at a relatively faster rate in the beginning of polymerization. Those active sites would minimize the interfacial energy barrier for the subsequent growth of polyaniline on the solid substrates. However, polyaniline nanofibers also form in the bulk solution simultaneously, resulting in rapid precipitate of polyaniline in the bulk solution. This consumes some reactive aniline cation-radicals and oligomeric intermediates, resulting in the reduction of the growth rate of polyaniline on the solid substrates, thus allowing polyaniline to grow only in a one-dimensional morphology from the active nucleation centers generated in the initial stage of polymerization.

4.5 MULTILAYER-TYPE NANOSTRUCTURES

Polyaniline has three different oxidation/reduction forms. Generally, standard chemical synthesis produces emeraldine salt. After dedoped by basic solution, emeraldine salt (ES) turns to emeraldine base (EB). When EB is exposed to oxidizers, it becomes pernigranilnine base (PB). The color of the films, powder or dispersion in EB form changes from blue to pink. The oxidation potential of pernigraninile oxidation state is \( \sim 0.8 \text{ V vs. SCE}^{[4,43]} \) which is sufficient to polymerize some monomers (e.g. pyrrole \( \sim 0.5 \text{ V vs. SCE}^{[4,44]} \)). Figure 4.19 shows the process to deposit polypyrrole on the surface
coated by aligned and oriented polyaniline nanofibers. After deposition of polypyrrole, the average size of the tips changes from 30nm to 120nm. It provides a possible route to synthesize the oriented nanostructures of other types of conductive polymers. These multilayer-type oriented nanostructures will have broad applicability in many areas.

Figure 4.19: Multilayer-type nanostructures fabricated by growing polypyrrole on the aligned and oriented polyaniline.
4.6 MOLECULARLY FUNCTIONALIZED POLYANILINE NANOFIBERS

Polyaniline nanofibers have been successfully synthesized through *dilute polymerization*\(^{[4.40]}\) and *porous membrane controlled polymerization*. Aligned and molecularly ordered polyaniline nanofibers are also simultaneously produced by these two methods. If we can modify the molecular structure of polyaniline nanofibers without damaging the nanostructures, this will broaden the applicability of polyaniline nanofibers.

Recently, there are some publications to functionalize solid-state polyaniline thin films or particles through the nucleophilic addition.\(^{[4.45-4.52]}\) Some nucleophilic reagents can be covalently bonding to the backbone of polyaniline such as sulfite (-SO\(_3^2\)\(^{-}\)), cyanide (-CN\(^{-}\)), carbanions, amines (-NH\(_2\)), thiols (-SH), arylsulfinate (C\(_6\)H\(_5\)SO\(_2\)\(^{-}\)), et.\(^{[4.45-4.52]}\) We examine a nucleophile, sodium metabisulfite (Na\(_2\)S\(_2\)O\(_5\)(aq)), on our synthesized polyaniline nanostructures. Figures 4.20 and 4.21 show that there is no apparent difference on the nanostructured morphology when polyaniline nanostructures are exposed to the nucleophile. UV/vis absorption spectra (Figure 4.22) show that fewer sulfonic groups are covalently bonded to EB polyaniline backbone comparing to 50% sulfonated EB polyaniline prepared by ~30% fuming sulfuric acid.\(^{[4.53-4.57]}\) According to the previous publication,\(^{[4.47]}\) only ~17% of sulfonation degree can be achieved when polyaniline emeraldine base is used as a precursor. UV/vis absorption pattern of polyaniline nanofibers after post-modification by sodium metabisulfite is in excellent agreement with the UV/vis absorption spectra of nonfibrous polyaniline powders of the similar sulfonation level.\(^{[4.47]}\)
Figure 4.20: Nucleophilic addition to polyaniline nanofibers.

Figure 4.21: Nucleophilic addition to aligned and oriented polyaniline nanofibers.
Figure 4.22: UV/vis spectra of polyaniline nanofibers after post-modification by nucleophilic addition (sodium metabisulfite).
REFERENCES: CHAPTER 4


CHAPTER 5

APPLICATIONS

5.1 SURFACE RESPONSE

In past decades, conductive polymers have been envisioned as important electronic materials\(^{[5.1-5.5]}\) for the semiconductor industry since they contain some of the properties of polymers, such as light weight, flexible bending, low driving energy, and low cost, etc. There were great possibilities for a wide range of applications, such as field-effect transistors\(^{[5.6-5.9]}\), pH sensors\(^{[5.10]}\), rechargeable batteries\(^{[5.11]}\), biochemical analysis\(^{[5.12]}\) and electrochromic devices\(^{[5.13]}\) as well as organic light-emitting diodes\(^{[5.14]}\).

A few studies on surface modification using conductive polymers have been published, especially for superhydrophobicity and superhydrophilicity. Most published works used low surface energy materials to modify the surface properties of conductive polymers, including fluoroalkanethiol molecules\(^{[5.15]}\), fluorinated dopant ions\(^{[5.16]}\) or polymerized fluorinated monomers\(^{[5.17,5.18]}\). However, those resulting films did not show superhydrophobic properties. Thus, G. Shi et al.\(^{[5.19]}\) used aligned polythiophene microtubules prepared by electrochemical template polymerization to enhance the hydrophobicity. Although the water contact angle on the surface of aligned microtubular
polythiophene was improved from $82^\circ$ to $134^\circ$, this resulting surface only can be attributed to be hydrophobic. Recently, Y. Yan et al. showed that polypyrrole film synthesized by electrochemical methods in the presence of the counter ion with low surface energy, e.g. perfluorooctanesulfonate, exhibited superhydrophobicity with a water contact angle of $152^\circ$.\textsuperscript{[5,20]} The films obtained can reversibly be switched between the superhydrophobicity and superhydrophilicity via controlling the oxidation and reduction states by electrical potential. In the electrochemical preparation, the substrates should be electrically conductive and inert to electrolyte solutions. It is almost impossible to deposit conductive polymers on an insulator or a relative large conductive substrate through electrochemical polymerization. Hence, chemical preparation should be a more versatile, scalable, feasible and favorable route to modify the surface properties of the solids. However, until now, no any publications address on the surfaces coating by conductive polymers with superhydrophobic or superhydrophilic properties via chemical preparation.

Herein, we report the first study on the superhydrophilic and superhydrophobic properties of aligned and oriented polyaniline nanofibers prepared by chemical oxidative polymerization.

### 5.1.1 Superhydrophilic Surface and Superhydrophobic Surface Fabricated by Aligned and Oriented Polyaniline Nanofibers

Aligned polyaniline nanofibers are successfully grown onto a variety of substrates of various sizes (Figs. 5.1(a)-5.1(b)). The surfaces coated by aligned polyaniline nanofibers show the property of superhydrophilicity with water contact angle less than 5
degrees (Fig. 5.1(c), inset). However, after exposure to CF₄ plasma, these same surfaces exhibit a dramatic change to superhydrophobicity and water contact angles higher than 175° (Fig. 5.1(d)). CF₄ plasma obviously lowers the surface energy. The same phenomenon is also observed on the multilayer-type nanostructures. Such novel coatings should provide a wider route to synthesize nanostructures of conductive, semiconductive, and non-conductive polymers for use in controlling the delivery of DNA via nanoneedle patches.

Figure 5.1: Aligned and oriented polyaniline nanofibers grown on (a) a bare-PET substrate (transparency), and (b) a substrate with micro-pattern pillars. (c) DNA is stretched on the superhydrophilic surface prepared by aligned polyaniline nanofibers. (d) A water droplet on the surface of CF₄-plasma-treated aligned polyaniline nanofibers. Inset (c) superhydrophilic surface and inset (d) superhydrophobic surface.
5.1.2 DNA Stretching on the Surface of Aligned and Oriented Nanofibers

We use the surfaces coated by aligned polyaniline nanofibers prepared by above two methods to stretch DNA. After the surfaces are coated by aligned polyaniline nanofibers, they show superhydrophilicity. This indicates that a water droplet will spread out on the surfaces with a contact angle less than 5°. When λ-DNA in aqueous solution is injected into the surfaces coated, λ-DNA is stretched by the strong capillary force resulting from the superhydrophilic surfaces (Figs. 5.1(c) and 5.2).

Figure 5.2: DNA stretching on the surface of aligned polyaniline nanofibers growth on PET.
5.1.3 Dual-Responsive Surface: Directly Patterned Surfaces with Superhydrophilicity and Hydrophobicity

We use a nucleophile (e.g. sodium metabisulfite) to modify the surface coated by aligned polyaniline nanofibers in base form. After nucleophilic addition, the surface still shows the superhydrophilicity because the functional group of sulfonate (-SO_3^-) covalent bonding to the backbone of polyaniline has higher surface energy (i.e. hydrophilic). When the entire surfaces are exposed to the acids with low surface energy (e.g. DBSA, fluorinated alkyl sulfonic acids, etc.), the modified area can not be redoped (or redoped negligibly) by such kind of acids. This creates superhydrophilicity on the modified area and hydrophobicity on the unmodified area (Fig. 5.3). This technique may be applied to write the patterns directly on the surfaces through the ink-jet printer. The resulting surface may be used to confine the stretched DNA in a certain area.

Figure 5.3: Direct patterning for the coated surfaces of aligned polyaniline nanofibers.
5.2 PATTERN BY PRINTER TONER: LINE-PATTERNING

The easy and cheap patterning method, i.e. line patterning,\textsuperscript{[5.21-5.23]} is used to demonstrate that aligned polyaniline nanofibers may be grown onto the pre-patterned substrates (Fig. 5.4). The line pattern is constructed by Microsoft PowerPoint 2000 SR-1 and printed by Hewlett-Packard LaserJet 4M on the over-head transparency film (PET). As shown in Figure 5.5, the thin film as deposited shows the morphology of aligned polyaniline nanofibers. After the removal of printer toner, there is no obvious change to the morphology of aligned nanofibers. This indicates that we may use this method to pattern aligned polyaniline nanofibers on a certain area for the applications on chemical sensors, biosensors, electronic devices, cell culture, etc.

Figure 5.4: Aligned and oriented polyaniline nanofibers are deposited onto the substrate with line patterning.
Figure 5.5: Aligned and oriented polyaniline nanofibers deposited on the over-head transparency patterned by line-patterning. The uncoated area results from the removal of the printer toner.
5.3 Chemical Sensor Fabricated by Polyaniline Nanofibers

We also demonstrate that polyaniline nanofibers can be used as a chemical sensor. Polyaniline nanofibers are synthesized by dilute polymerization from 1M HClO$_4$(aq) at room temperature. The diameters of the nanofibers ranges from 72 to 250nm. The nanofiber network used for the sensor is shown in Fig. 5.6. As-synthesized nanofibers are \textit{in-situ} doped by HClO$_4$ and then dedoped by 0.1M NH$_4$OH(aq) to prepare emeraldine base (EB) form of the nanofibers. The EB form of the nanofibers is redoped by 1M HCl(aq) to form conductive polyaniline nanofibers. The conductive polyaniline nanofibers redoped by HCl are used for the demonstration of the chemical sensor. Thin films of polyaniline/HCl nanofibers of dimension (0.5cm (width) $\times$ 1.2cm (length) $\times$ 10$\mu$m (thickness)) are cast onto glass substrates from the suspension of the nanofibers in 1M HCl(aq). Two gold wires separated by 1cm and mounted on the sample using carbon paste. A droplet of 30% w/w NH$_4$OH(aq) is placed 3-cm away from the device in the petri disk. The current (A) of the device with the applied voltage 0.7V is monitored before and after a droplet of 30% w/w NH$_4$OH(aq) is placed in the disk. As shown in Figure 5.6, the preliminary results show that the sensor fabricated by polyaniline nanofibers responds very fast to NH$_4$OH vapor. The resistant increases when the sensor is exposed to NH$_4$OH vapor. Such fast response results from the extremely high surface area and the porous structures of nanofibers\textsuperscript{[5,24]} enabling the rapid dedoping of the bulk of the fibers as evidenced by a simultaneous change the reflection color from green to blue. The study can also be performed by the optical or electrochemical study as well as electric study.
Figure 5.6: Chemical sensor fabricated by polyaniline nanofibers synthesized by dilute polymerization from 1M HClO₄(aq) at room temperature.
REFERENCES: CHAPTER 5


CHAPTER 6

CONCLUSION

This thesis only gives a brief overview and summary of our current research and development on the nanostructures of polyaniline in recent years. The nanostructures of conductive polymers offer a promising opportunity for the improvement and the development of various types of industrial products. Fundamental research on the control of the growth of 1-D nanostructures of conductive polymers has just begun. There are still many undiscovered potential applications of nanostructured conductive polymers in the fields of chemistry, physics, biology and engineering. Further investigations are needed and expected.
BIBLIOGRAPHY

CHAPTER 1


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### CHAPTER 3


### CHAPTER 4


CHAPTER 5


