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“Deposition of Ultrathin functional Films on Nanoparticles and Nanotubes by Plasma treatment”

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Deposition of Extremely Thin Functional Films on Nanoparticle/Nanotube Surfaces by a Plasma Treatment

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ABSTRACT

There has been an increasing need and great interest in both the fundamental science and the cutting-edge technology to modify the surfaces of nanoparticles. Such a surface modification must be done at the nanoscale in terms of structure, composition, and uniformity. The great challenge therefore lies critically on the deposition of a film on the order of a few nanometers on the surfaces of the nanoparticles. In this thesis, the uniform deposition of ultrathin polymer films of 2-10 nm on the surfaces of nanoparticles and nanotubes by plasma polymerization was demonstrated. The deposited film can also be tailored to different compositions. High Resolution Electron Microscopy (HREM), Time-of-flight Secondary Ion Mass Spectroscopy (TOF-SIMS), Infrared Spectroscopy (IR) and other tests were used to confirm the polymer coating on the nanoparticle/nanotubes surfaces. Other tests, such as Contact Angle and ion exchange, were used to test the surface properties of the modified nanoparticles. Plasma processing opens a window for altering the intrinsic properties of materials that cannot be achieved by conventional methods and materials.

Keywords: plasma polymerization, nanotechnology, coating
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Chapter 1: INTRODUCTION

1.1 General Background

Powders, including carbon black, zinc oxide, ferric oxide, alumina, and silica, are useful raw materials in the rubber, electronic, paint, and biomaterial industries. The surface properties of powders are a very important factor when powders are used in the industrial applications. How to modify the surface of powder to improve the adhesion and functionalize the powder surface will be the key for the powder industry.

Taking different film technologies into consideration, plasma polymerization coating as well as plasma surface treatment of powders is particularly promising because of the following unique features and advantages. (1) The starting feed gases used may not contain the type of functional groups normally associated with conventional polymerization; (2) Such films are often highly coherent and adherent to a variety of substrates, including conventional polymers, glasses and metals; (3) Polymerization may be achieved without the use of solvents; (4) Plasma polymer films can be easily produced with thickness from several nanometers to 1µm; (5) through careful control of the polymerization parameters, it is possible to tailor the films with specific chemical functionality, thickness, and other chemical and physical properties.

In contrast to flat (wafers, panes of glass, solar cells, foils, cloth) or lumpy (cutting tools, lenses, reflectors) substrates, there is still no satisfactory plasma treatment process for powders and granules because the handling of powders in a plasma apparatus is very difficult. The difficulty comes from the nature of powders: they have a very small diameter and very large
surface area. More over, powders tend to coagulate which makes uniform and efficient treatment more difficult. This inherent difficulty is also present with plasma surface treatment of powders and provides probably the toughest technological challenge in the plasma process.

1.2 Why nanoparticles

What is particularly exciting in the study of nano-particles, nano-structured materials, and nano-devices is their ability to add value to materials and products through enhancement of specific properties, such as the following:

Big special surface area: Compared with micro or macro scale size particles, nanosize particles have much greater surface area for the same volume of material. Usually decreasing the particle size by one order of magnitude will increase the surface area 10 times if we keep the volume as constant. This large surface area will be very useful when we use the particles as substrates.

Discontinuation of electron energy gap: According to the famous Kubo theory \(^{[1,2]}\), the energy gap of electron will increase with the particle size decreasing, according to the relationship:

\[
\delta = 4E_f/(3N) \propto V^{-1}
\]

In this equation, \(E_f\) is energy of Fermi level; \(N\) is the number of atoms in the particle; \(\delta\) is the energy gap. From this equation, when the materials size is large (micro or even bigger), \(\delta\) will be 0, which means the energy is continuant. But when the particles size decreases to the nano level, we could not think \(N \rightarrow \infty\), so \(\delta\) will not be 0 any more. This different will change a lot of properties of materials.
Mechanical strength: Nano-structured powders have been produced by plasma processing where the reactor vaporizes coarse metal particles; \([^3]\) by combustion synthesis where redox reactions take place at elevated temperatures, followed by quenching; and by mechanical alloying with gas atomization. When nanocrystalline powders achieved by these means are compacted and applied as a coating, they lend significant strength and ductility to a variety of conventional materials such as ceramic, composites, and metal alloys.

Superconductivity: This involves a deposition of nanocrystals on substrates, leading to improved optical and electrical properties. \([^4]\)

Covering power: Because nanostructuring increases the number of active sites—there are many more atoms per grain boundary—the enhanced surface area leads to a reduced material requirement, which in turn can lower cost. \([^5]\)

Ability to incorporate high cost materials: Expensive materials such as colorants and drugs may be effectively dispersed in small and controlled quantities through nanostructuring. \([^6]\)

Thus, nanostructured materials can significantly reduce material costs and improve performance and functionality in a large variety of applications.

1.3 Plasma Polymerization

1.3.1 Mechanism of Plasma Polymerization

Plasma Polymerization is a relatively new material preparation process and is widely used recently, especially in the semi-conductor industry. The materials formed by plasma
polymerization are vastly different from conventional polymers and constitute a new kind of material.

In general, plasma polymerization is well represented by a bi-cyclic step-growth mechanism \cite{7} as show in Figure 1.1:

Here i, j and k merely indicate the difference in the size of species and M* represents a mono-functional reactive species which can be an ion of either charge, an excited molecule, or a free radical, produced from a neutral species M but not necessarily retaining the molecular structure of the starting material. Also, M can be a fragment, or even an atom detached from the original starting material. Here M* represents a di-functional activated species.

As shown in the above cycles, the overall reaction contains two major routes of rapid step growth. Cycle 1 is via the repeated activation of reaction products from mono-functional activated species. Cycle 2 is via di-functional or multifunctional activated species, which produced very possibly branches or cross-links in the polymer structure. This may explain why plasma polymers are usually cross-linked. In both cases, the growth mechanism of polymerization is rapid step-growth polymerization.

The total reaction rate shown in the above cycles should be a function of electron density and electron energy and can be expressed as;

\[ R_{\text{total}} = f(N, E) \]
Where $R_{\text{total}}$ is the total reaction rate, $N$ is the electron density and $E$ is the electron energy. It can be observed that the rate of each reaction depends on the concentration of reactive species, $M^*$ or $^*M^*$, which are generated due to the plasma excitation.

Unlike conventional polymerization, most of the reactions in plasma polymerization are one-step reactions between two reactive species. Some other reactions are between an activated species and a molecule, which are essentially the same as the propagation reaction of the conventional addition polymerization. Such reactions can proceed in a chain mechanism if the reacting molecule has the appropriate molecular structure. However, even in such cases the formation of polymerization is because of the very low ceiling-temperature of addition polymerization in vacuum.

Plasma polymerization is usually initiated and generated in the vapor phase during the plasma process. As polymerization proceeds, the growing polymer can not remain in the vapor phase and diffuse to a surface. Reactive species in the gas phase, such as ions and free radicals, may simultaneously interact with surfaces inside the plasma reactor that have been activated by the impact of the glow discharge to form ions or free radicals from the surface molecules of substrates. Plasma polymer film deposition and growth steps on that surface may follow.

The homogeneous polymerization in the plasma phase and heterogeneous polymerization at the surface of the growing film can be summarized by the reaction scheme proposed originally by Poll et al. \[8\] and illustrated in Figure 1.2. As shown in this figure, the gaseous precursor monomers can polymerize in the plasma and deposit as a film (reaction path 1, characterized by a rate $k_1$), be converted in the plasma into reactive products (path 2), or be converted in non-
reactive products (path 4). The reactive products can convert into depositing polymer film (path 3) or can be converted to non-reactive products (path 5). Degradation of the formed polymer film can occur to form non-reactive products (path 6).

Path 1, by which the monomer is directly polymerized into the growing film, is also called plasma induced polymerization. This is essentially a conventional molecular polymerization process, triggered in this case by reactive plasma species. Plasma induced polymerization can take place only if the original monomer contains polymerizable functional groups, such as double, triple, or cyclic bonds. [9]

Deposition of a polymer film through path 2 and 3 is plasma polymerization. In plasma polymerization the intermediate reactive products can be ions, excited molecules, and free radicals not necessarily preserving the original monomer. The monomer does not need to have polymerizable groups to undergo plasma polymerization.

1.3.2 Plasma Polymerization Reactor

Based on the electrical sources used, there are three types of plasma reactors for plasma polymerization of organic monomers. Radio frequency (RF) (usually 13.56M Hz) and microwave (MW) (2.45G Hz) are mainly used when the substrates are insulating materials. DC reactor, which has a direct current source, is simpler than the other two and would be the best one for electric conductive substrates. The substrates can act as electrodes of the DC reactor. Currently, the RF reactor is the most popular plasma reactor, because the MW reactor is too complicated and DC has some restrictions about the substrates.
1.3.2.1 DC reactor

In DC plasma reactors, the plasma is sustained between two parallel plate electrodes as Figure 1.3, and the electric power is supplied to excite the plasma in the abnormal discharge mode. The distances between the electrodes and the pressure in the reactor have to satisfy Paschen’s law. [10]

\[ V_b = \frac{C_1 (pd)}{C_2 + \ln(pd)} \]

\( p = \) the pressure of gas;
\( d = \) distance between electrons;
\( C_1 \) and \( C_2 = \) constants that change with the nature of the gas; and
\( V_b = \) the breakdown voltage.

The power supplies used to sustain DC plasma can generally be used in a constant voltage, constant current, or constant power mode. The power supplies should be able to control the preset value in each mode. The excitation and sustainment of a DC plasma require the use of electrically conductive electrodes and samples. However, electrically insulating films may deposit locally on the surface of the electrodes or samples due to contaminants formed in the plasma. In such cases, local dielectric breakdown normally occurs, causing arcing that results in spikes of high currents.

The power supply must be able to withstand these spikes and return to normal operation without shutting off. However, it must also be able to distinguish between the transient arcing currents and shorts that may occur between the electrodes and grounded surfaces. This feature, called arc suppression, must be a characteristic of a DC power supply of a plasma reactor.
1.3.2.2 RF reactor

RF discharges have many advantages over DC discharges, which explains the wider use of RF plasma as compared to DC plasma:

1. RF plasma can be excited and sustained using either conductive or non-conductive electrodes, while DC discharges require the electrodes to be conductive throughout the process.

2. RF plasma can be sustained with internal as well as external electrodes, while DC discharges require the electrodes to be inserted inside the reactor and be in direct contact with the plasma. Use of external electrodes is sometimes required when the gases of the discharge are corrosive or when one wants to reduce contamination of the plasma with the material of the electrodes.

3. RF plasmas are characterized by higher ionization efficiencies than the DC plasma.

4. RF plasma can be sustained at lower gas pressures than DC plasma.

5. In RF plasma the energy of the ions bombarding the sample is controlled by the negative bias, which can be adjusted over a wide range of values. Samples placed on the cathode of the DC discharge are exposed to bombardment of high-energy ions that are accelerated at voltages that have to be above the minimal breakdown voltage. This can cause damage to sensitive substrates.

A typical RF-plasma system is shown in Figure 1.4. These kinds of reactors couple the RF power to two parallel electrodes inserted inside the reactor. The coupling is done through special RF vacuum feedthroughs. One electrode is often grounded together with the walls of
reactor. This arrangement is also called a diode or parallel plate reactor. This is the most common approach in the design of industrial RF plasma reactors, but it is not suitable for the powder treatment.

**Stirred reactors**

Figure 1.5 [11] shows a low temperature plasma-treating system based on the stirring principle. Powders are placed in the Pyrex reactor, which is then evacuated. Gases pass through the reactor at a certain flow rate. The sample is smoothly stirred by rotating the stirring fin connected to a motor through an airtight seal while radio frequency is applied under the specified pressure. The plasma conditions are maintained while treating the sample. The rotating speed for agitating the sample is set at around 10 rpm. Typical problems with stirred reactors include treatment homogeneity and treating capability per batch.

There are several other types of plasma reactors for powder treatment that have been developed [12, 13, 14, 15]. Using those reactors, good results were obtained for the improvement of the properties of powders.

**1.3.2.3 Microwave reactor**

Microwave plasmas are sustained by power supplies operating at a frequency of 2.45 GHz. This frequency, which is commonly used for industrial or home heating applications, makes suitable power supplies readily available. The excitation of the plasma by microwaves is similar to the excitation with RF, while differences result from the ranges of frequencies.
In a typical microwave plasma the strength of the electric field is about $E_0 \sim 30\text{V/cm}$; therefore, in a collisionless situation, the maximum amplitude of the electron at microwave frequencies is $x < 10^{-3} \text{cm}$, and the corresponding maximum energy acquired by an electron during one cycle is about $0.03\text{eV}$.\[16\] This energy is far too small to sustain a plasma. Therefore microwave discharges are more difficult to sustain at low pressures ($< 1\text{torr}$) than DC or RF discharges.

In a collisional discharge, the absorption of microwave power is a function of the collision frequency of the electrons with the heavy species and is therefore dependent on the pressure in the discharge. For a microwave frequency of $2.45\text{GHz}$, efficient microwave absorption in helium occurs at $5-10 \text{ torr}$\[17\]. For other gases, the optimum pressure for microwave discharge is in the range $0.5-10 \text{ torr}$.

While the RF glow discharge can be made to extend virtually throughout the entire reactor, whose dimensions are much smaller than the wavelength of the RF field ($\sim 22 \text{ m at 13.56MHz}$), the microwave plasma has its greatest glow because of the coupling microwave cavity and diminishes rapidly outside it, because of the much smaller wavelength of the microwave ($X = 12.24 \text{ cm for a frequency of 2.45GHz}$). In the microwave plasma, the magnitude of the electric field can vary within the reactor, which now has dimensions of the same order of magnitude as the wavelength. One can thus find active species from the discharge still persisting into a region free of the glow of the plasma, that is, in afterglow.
Microwaves are easily absorbed or reflected by most materials and cannot be transmitted via cables, like RF energy, without significant losses. Special coaxial cables can be used to transmit low-power (<200 w) microwaves. The coax consists of two concentric conductors separated by a dielectric. For higher-power levels, specially designed wave-guides have to be used. The cross sections of the conductors of the coax or the waveguide are determined by the wavelength of the microwave\textsuperscript{[18]}.

A microwave power supply system used for microwave is illustrated in Figure 1.6 and consists of

1. A filtered, low-ripple microwave power supply of constant frequency but variable power.
2. A circulator, whose role is to protect the power supply from large reflected power which may result from an impedance mismatched microwave applicator.
3. Meters for monitoring both the incident and reflected power.
4. A variable, manual or automatic, impedance matching of the applicator with the plasma, at different and variable discharge conditions; an impedance mismatch will cause the microwave to reflect instead of propagate into the plasma.

1.4 Current Research Status

1.4.1 Polymer film coating on a plane substrate by plasma polymerization

There are several ways to prepare ultrathin films, including LB (Langmuir-Blodgett) techniques and thermal evaporation of volatile organic compounds. Both techniques are well-
known as to their advantages and their problems. For these two methods, the continuity and the mechanical properties of the films are the main problem. For example, LB film of PMMA, having a thickness of 14nm, contains pinholes on the order of about 10 defects per square centimeter. \cite{19} Although this method is much better than spin coating, there are still too many defects.

Besides the wet techniques, electron beam, and UV irradiation of organic vapors have been used to coat ultrathin films on the substrates. However, the thickness of the films using these methods are usually above 20nm. In 1993, K. Senda \cite{20} used plasma technique to coat Si wafers and successfully got very uniform films under 10 nanometers in thickness. The deposition conditions he used are: a discharge frequency 13.56 MHz, a pressure range 0.5-0.8 Torr and acetylene (C\textsubscript{2}H\textsubscript{2}) was used as the monomer.

Figure 1.7 shows the distribution of the thickness of the deposited film in the gas flow direction, as measured by an ellipsometer. It’s shown in Figure 1.7, in the gas flow direction the deposition ratio changes with distance. This result provides some hints that the film thickness can be controlled by controlling the operation parameters.

Figure 1.8 (a) and (b) show cross-sectional AFM images of a Si substrate and that of 5-nm-thick film, respectively. The root mean square (rms) roughness of the Si is 0.27nm and the rms of the polymer film is 0.55nm. The surface roughness appeared to be the same when compared with the wafer’s surface roughness. For the ultrathin films examined by AFM, no pinholes were found even with the highest atomic scale resolution.
1.4.2 Polymer film coating of particles by plasma polymerization

Compared with flat substrates, there are very few reports on such deposition on powdered substrates. Several studies reported work on cold plasma treatment of mica or silica used in engineering plastics. \cite{21, 22, 23} Vollath and Szabo reported polymer coating of PMMA on Fe$_2$O$_3$ particles using a microwave plasma synthesis technique \cite{24}. In their experiment, the monomer condensed at the surface of the particles and polymerized under the influence of the UV radiation generated by the MW plasma used to create the iron oxide particles. However, in their process, the coating polymer occupied about 80 vol.% of the coated particles. Therefore, the experiment should not be described as coating, but rather as an embedment of ceramic cores in the matrix of a polymer matrix. Inagaki \cite{25} reported surface modification of polyethylene powders using plasma reactor with fluidized bed. They discovered that the oxygen plasma treatment of the polyethylene powder in the fluidized bed showed a capability that the surface of the powder was changed from hydrophobic to hydrophilic. Anders \cite{26} studied the film synthesis on powders by cathodic arc plasma deposition. They coated Al$_2$O$_3$ powders with platinum, the powder particles were moved during deposition using a mechanical system operating at a resonance frequency of 20 Hz. Analyses shown that all particles are completely coated with a platinum film have a thickness of about 100 nm and the deposition rate was very high because of the short deposition time.

1.5 Applications for the Plasma Surface Treatment of Powders

Plasma treated powders have a wide range of potential applications. The applications involve improving the following properties of powders: biocompatibility, sorption, wettability,
triboelectricity, barrier and insulation, adhesion, diffusion, friction coefficient, corrosion, dispersion, flowability, and so on.

One of the large markets for plasma treatment application is pharmacology. With the help of plasma coating, pharmaceuticals can be finely dispersed on the nano surface thus offering rapid drug delivery and reduced dosages for patients. In the medical area, plasma treated particulates can also be used for artificial joints with an enhanced surface biocompatible property.

Plasma treatment also has wide applications in area other than medical and pharmacy such as the pigment industry, rubber chemistry and others.

1.6 Project Objective

As mentioned before, the current research about plasma treatment of particles is mainly focused on Micro size or even larger. Almost no papers report about the research about the coating on the nanosize particles. The main objective of this project is to develop a complete set of techniques for plasma thin film coating on nanoparticles. In order to investigate the probability of this technology, several nanoparticles have been chosen. The particles not only include 0 dimension particles such as NiFe$_2$O$_4$, ZnO, YbErO$_2$S, but also include one dimension nanomaterials such as Multi-wall Carbon Nanotubes (MWCNT).

After the coating, several characterization methods were used to test the coating film. The methods used here include TEM, FTIR, SIMS and so on. For each different particles, other
special test methods were used to investigate the surface properties of particles, which include Contact Angle (CA), Ion exchange, solubility.

Since plasma polymerization is a highly system-dependent process, a comprehensive study of the operation parameters of a plasma reactor is needed. The objective is to determine the influences of operation parameters on the deposition rate and the chemical structure and properties of plasma-polymerized films. These parameters usually include: (1) the configuration of the system, (2) deposition time, (3) input power, (4) the working pressure, (5) the volume ratio of different monomers, (6) the monomer types. Most of these parameters have been reported to affect deposition rates and the properties or structure of the deposition films. Understanding the effect of each parameter on the plasma polymerization processing will facilitate optimizing the processing by optimizing the combination of different operation parameters in a given circumstance.
CHAPTER 2: EXPERIMENTAL MATERIALS AND METHODS

2.1 Materials

In this research, the substrates used for plasma deposition include ZnO, NiFe_2O_4, YYbErO_2S, and Carbon Nanotube. The ZnO powders are from the Zinc Corporation of American in Monaca, Pennsylvania, USA. The NiFe_2O_4 is from the Inframat Corporation in Willington, CT, USA. The YYbErO_2S is from the OraSure Technologies, Inc in Bethlehem, PA, USA. The carbon nanotube Pyrograf-III PR-24 is from Applied Science Inc located in Cedarville, Ohio, USA. The monomers used for plasma coating include Pyrrole, Styrene, C_6F_14 and Acrylic Acid.

Pyrrole of 98% purity was obtained from Aldrich Chemical Company Inc, Milwaukee, Wisconsin. Pyrrole has the following chemical structure:

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  N
 /|
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Styrene of 99.5% purity was obtained from Alfa Aesar, A Johnson Matthey Company, Ward Hill, MA. Styrene has the following chemical structure:
Methyl Methacrylate (MMA) of 99.0% purity was obtained from Alfa Aesar, A Johnson Matthey Company, Ward Hill, MA. Methyl methacrylate has the following chemical structure:

Acrylic Acid of 99.5% purity was obtained from Alfa Aesar, A Johnson Matthey Company, Ward Hill, MA. Acrylic Acid has the following chemical structure:

C6F14 of 95+% purity was obtained from Alfa Aesar, A Johnson Matthey Company, Ward Hill, MA. Potassium bromide (KBr) of 99+% purity was obtained from Aldrich Chemical Company Inc, Milwaukee, Wisconsin.

2.2 Characterization Techniques for Treated Powders

2.2.1 Transmission Electron Microscopy (TEM)
In TEM, a thin solid specimen ($\leq 200$ nm thick) is bombarded in a vacuum with a highly focused, monoenergetic beam of electrons. The beam is of sufficient energy to propagate through the specimen. A series of electronmagnetic lenses then magnifies this transmitted electron signal. Diffracted electrons are observed in the form of a diffraction pattern beneath the specimen. This information is used to determine the atomic structure of the material in the sample. Transmitted electrons form images from small regions of the sample that contain contrast, due to several scattering mechanisms associated with interactions between electrons and the atomic constituents of the sample. Analysis of transmitted electron images yields information both about the atomic structure and about defects present in the material. The lateral resolution is better than 0.2 nm on some instruments [27].

A JEOL JEM 4000EX TEM instrument is used to acquire the image of uncoated and coated samples. The original and coated samples were dispersed onto the holy-carbon film supported by Cu-grids for the TEM operated at 400 kV.

2.2.2 Secondary Ion Mass Spectrometry (SIMS)

Secondary ion mass spectrometry, SIMS, is the mass spectrometry of ionized particles which are emitted when a surface, usually a solid, is bombarded by energetic primary particles which may be electrons, ions, neutrals or photons. The emitted or ‘secondary’ particles will be electrons; neutral species atoms or molecules or atomic and cluster ions. The vast majority of species emitted are neutral but it is the secondary ions which are detected and analyzed by a mass spectrometer. It is this process which provides a mass spectrum of a surface and enables a detailed chemical analysis of a surface or solid to be performed.
TOFSIMS analysis is performed on a Kratos Prism spectrometer. This instrument is equipped with a reflection-type Time-of-Flight mass analyzer and pulsed 25kv primary source of monoisotopic $^{69}$Ga$^+$ ions, with a minimum beam size of 500 Å. Positive and negative spectra are collected at 25kv primary ion energy, a pulse width of 25ns and a total integrated ion dose of $\sim$10$^{11}$ ions/cm$^2$. This is well below the generally accepted limit of $\sim$5X10$^{12}$ ions/cm$^2$ for the static SIMS condition of organic materials [28]. Under these conditions a mass resolution $M/\Delta M$ of 8,000 at m/z=+27 amu could be obtained. For each sample, at least three different regions are analyzed. The powders were stored in ambient conditions after plasma polymer film deposition prior to analysis.

2.2.3 Infrared Spectroscopy

FTIR spectra are acquired on a BIO-RAD FTS-40 FTIR spectrometer with a BIO-RAD transmittance attachment. The spectra are obtained using a resolution of 8cm$^{-1}$ and are averaged over 128 scans. A background spectrum obtained with an uncoated KBr pellet is subtracted from the acquired spectra in all cases.

Infrared spectroscopy provides information on the structure of the deposited plasma polymer films, i.e. the functional groups of the films.
Chapter 3: EXPERIMENTAL RESULT

3.1 Pioneering work

3.1.1 Plasma Polymer Films Deposited on ZnO Particles

A RF-plasma reactor was used for the particle coating. The schematic diagram of the plasma reactor for thin film deposition of particles is shown in Figure 3.1. The vacuum chamber of the plasma reactor consists of a long Pyrex glass column about 80 cm in height and 6 cm in internal diameter. The process parameters are summarized in Table 3.1.

Table 3.1. Processing parameters of RF-plasma coating of polymer on nano zinc oxide powders

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma Power (W)</td>
<td>10-80</td>
</tr>
<tr>
<td>Base pressure, (mTorr)</td>
<td>100 mTorr</td>
</tr>
<tr>
<td>Total gas pressure, (mTorr)</td>
<td>300 – 450 mTorr</td>
</tr>
<tr>
<td>Monomer/Precursor Gas</td>
<td>Acrylic acid, pyrrole</td>
</tr>
<tr>
<td>Deposition duration</td>
<td>15min to 2 hours</td>
</tr>
<tr>
<td>Deposition Temperature</td>
<td>Ambiance</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>Powder/particle size</td>
<td>ZnO 100-400 nm</td>
</tr>
<tr>
<td>Polymer coating thickness</td>
<td>10-20 nm</td>
</tr>
<tr>
<td>Stirring method</td>
<td>Magnetic Stirring</td>
</tr>
</tbody>
</table>

The zinc oxide powders are vigorously stirred at the bottom of the tube and thus the surface of particles can be continuously renewed and exposed to the plasma for thin film
deposition during the plasma polymerization processing. A magnetic bar was used to stir the powders. The gases and monomers were introduced from the gas inlet during the plasma cleaning treatment or plasma polymerization. The system pressure was measured by a thermal-couple pressure gauge. A discharge by RF power of 13.56 MHz was used for the plasma film deposition. Before the plasma treatment, the basic pressure was pumped down to less than 100 mtorr and then the carrier gas (such as argon) or monomer vapors were introduced into the reactor chamber. The operating pressure was adjusted by the gas/monomer mass flow rate. Pyrrole or Acrylic Acid was used as monomers for plasma polymerization. During the plasma polymerization processing, the input power was 10-80 W and the system pressure was 300-450 mtorr. The input power was justified by the matching box, which connected between the plasma generator and the coil. The plasma treatment time was 15 to 120 mins according to the different monomers and the different film thickness desired. Per batch, 10-20 grams of powder was treated.

After the plasma treatment, the zinc oxide powders were examined by using Transmission Electron Microscopy (TEM), Secondary Ion Mass Spectrometry (TOFSIMS), and Infrared (FTIR). The high-resolution TEM (HRTEM) experiments were performed on a JEOL JEM 4000EX TEM.

3.1.2 Microstructure of the Coated Powder

In transmission electron microscopy, the original and coated ZnO nanoparticles were dispersed onto the holy-carbon film supported by Cu-grids for the TEM operated at 400 kV. Figure 3.2 shows the HRTEM image of the original, uncoated ZnO particles. As can be seen in
Figure 3.3 and Figure 3.4 are the HRTEM images of the coated particles. Compared to Figure 3.2, a bright ring was found around the particles. From higher magnification images, the bright ring was found to be one kind of amorphous layer outside the lattice structure. The ZnO particles have the crystalline structure. So the lattice structure in the images will be the ZnO particles substrate. The amorphous layer which does not appear in the uncoated image (Figure 3.2) can be used to prove that the observed layer is due to the coating rather than an artifact in TEM observation. Figure 3.3 and Figure 3.4 have the high magnification images showing a uniform coating on the particle surfaces. The coating thickness is approximately 10-20 nm thick over the entire particle surface. Particularly interesting, although the shape of particles is non-spherical, and at some places the shape is even very sharp, the coating remains the same thickness. This shows that the plasma chamber produce a uniform coating on particles.

3.1.3 EDS Analysis

Typical EDS spectra of coated and uncoated samples are shown in Figure 3.5 (a) and Figure 3.5 (b). After plasma coating, the peak of Zn and Cu decreases and the carbon peak increases sharply, indicating the outside layer has different compounds compared with the ZnO particles. This observation further proves the surface is a new layer rather than an artifact in the TEM observation. In the spectrum, some Fe and Cu peaks can be found. These elements are impurities, which used to dope the ZnO to increase the conductive property of the ZnO particles.
3.1.4 FTIR Spectra Analysis

For the FTIR experiment, potassium bromide (KBr) of 99%+ purity was obtained from Aldrich Chemical Company Inc, Milwaukee, WI. The KBr powder was pressed into small pellets for the FTIR experiment. FTIR spectra were acquired on a BIO-RAD FTS-40 FTIR spectrometer with a BIO-RAD transmittance attachment.

(1) Poly-pyrrole coated ZnO

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3340</td>
<td>N-H stretching vibration of primary and secondary amines</td>
</tr>
<tr>
<td>1620</td>
<td>C=C conjugated and C=N conjugated stretch and N-H deformation vibration</td>
</tr>
<tr>
<td>1420</td>
<td>Alkane C-H deformation region</td>
</tr>
<tr>
<td>1024</td>
<td>C-N stretching vibration</td>
</tr>
<tr>
<td>740</td>
<td>C-H out of plane bending</td>
</tr>
</tbody>
</table>
Table 3.3: Peak assignments for the Polypyrrole films of Figure 3.7

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3374</td>
<td>N-H stretching vibration of primary and secondary amines</td>
</tr>
<tr>
<td>2963</td>
<td>Asymmetric and symmetric C-H stretching vibration of saturated hydrocarbons</td>
</tr>
<tr>
<td>2934</td>
<td></td>
</tr>
<tr>
<td>1620</td>
<td>C=C conjugated and C=N conjugated stretch and N-H deformation vibration</td>
</tr>
<tr>
<td>1420</td>
<td>Alkane C-H deformation region</td>
</tr>
<tr>
<td>790</td>
<td>C-H out of plane bending</td>
</tr>
<tr>
<td>725</td>
<td>C-H out of plane bending (cis –C=C-) and –(CH₂)ₙ, n&gt;3 rocking vibration</td>
</tr>
</tbody>
</table>

Comparing Figure 3.6 with Figure 3.7, the IR spectrum of the plasma coated PPy is much more complicated than the IR spectrum of the pyrrole monomer. Both spectra exhibit a strong peak at about 3300cm⁻¹, which is due to the N-H bond stretching vibration of primary and secondary amines and imines. In Figure 3.6 and Figure 3.7, the absorption around 1640cm⁻¹ corresponds to the amines in the pyrrole structure. At about 2963.38cm⁻¹ and 2934.44cm⁻¹, there are two peaks in Figure 3.7, but not in Figure 3.6. The peak at 2963.38cm⁻¹ is Asymmetric CH₃ stretching and the peak at 2934.44cm⁻¹ is asymmetric CH₂ vibration. Both peaks are corresponds to the stretch vibration of saturated hydrocarbons. The structure of pyrrole is following:
In the molecular structure of the pyrrole monomer, all the Carbon atoms are unsaturated. There are no -CH₃ and –CH₂- function groups in the pyrrole molecule. Thus, the peaks around 2900 cm⁻¹ come from the plasma coating processing. After plasma processing, the function groups –CH₃ and –CH₂-were introduced into the molecular structure and these two function groups only can come from the amine ring being broken and subsequent polymerization. There is another special peak around 722 cm⁻¹ appearing in Figure 3.7, but not in Fig 3.6. This peak usually belongs to –(CH₂)ₙ unites. Only when n>4, the peak will appear around 720 cm⁻¹, otherwise it will shift to low frequency. All of these differences show the film produced by the plasma polymerization is no longer original pyrrole. The monomer has been polymerized in the plasma treatment.

(2) Poly (acrylic acid) coated ZnO

**Table 3.4: Peak assignments for the PAA films of Figure 3.8**

<table>
<thead>
<tr>
<th>Frequency cm⁻¹</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3460</td>
<td>O-H stretching vibration</td>
</tr>
<tr>
<td>2963</td>
<td>Asymmetric and symmetric C-H stretching vibration of saturated hydrocarbons</td>
</tr>
<tr>
<td>2934</td>
<td></td>
</tr>
<tr>
<td>1720</td>
<td>C=O stretching vibration</td>
</tr>
<tr>
<td>1408</td>
<td>O-H winding vibration</td>
</tr>
<tr>
<td>1265</td>
<td>C-O stretching vibration</td>
</tr>
</tbody>
</table>
Figure 3.8 shows the FTIR spectrum of plasma coated ZnO. As can be seen in this figure, there is a very strong peak around $1700\text{cm}^{-1}$, which is the special stretching vibration absorption of the C=O function group. At $3460\text{cm}^{-1}$, there is a small peak. This is the special absorption of the O-H function group. If the polymer has the COOH function group, the peaks around $3400\text{cm}^{-1}$ and $1700\text{cm}^{-1}$ will both be very strong. In this spectrum, only the peak around $1700\text{cm}^{-1}$ is very strong and the peak at $3400\text{cm}^{-1}$ is actually very weak, which means the polymer film contains the C=O function group not the COOH function group. In order to investigate the effect of power, several different power levels have been used, including: 15w, 30w, 60w, and 80w. Because the special absorption appeared around $1700\text{cm}^{-1}$, the FTIR spectra of each power level have been put together at this range as shown in Figure 3.9

In Figure 3.9, the peaks of C=O become stronger as the plasma power increasing. But compared to the spectra at 60w and 80w, there is almost no change at all.

3.1.5 Contac Angle Test

In order to investigate the surface property of the plasma film, the contact angle test is used to prove the film is hydrophobic or hydrophilic. The metal sheets are put at the same position and the same condition as the powder treatment. After plasma treatment, the metal sheets are used to test the contact angle by A VCA 2000 video contact angle system.

With the plasma power increasing, the contact angle of the polymer film decreases firstly, then increases. When the power level higher than 60w, the contact angle does not change any
more. Figure 3.10 further proves the function group in the polymer film is C=O not COOH.

When the power level is very low, there will be some O-H function groups attached to the film. The OH function group will increase the hydrophilic property of the surface. Therefore, the contact angle decreases. With the power level increasing, the weak bonding between the C-OH will be broken by electrons. The coating will then become more hydrophobic. Therefore, the contact angle increases. After power level reach 60 w, the contact angle becomes nearly constant with the power level.

3.1.6 Solubility

In order to investigate the solubility of the plasma film, the coated steel plates were put into water for 1 hour, then they were dried them. The FTIR spectra before and after the water treatment were compared at low power 15 and 30 w, and the peaks almost disappear after the water treatment. The FTIR spectra of after the water treatment are only straight lines and almost no peaks appear in the spectrum. From the FTIR result, we can say that after water treatment, the polymer films have totally disappeared and dissolved into water. When power is increased to 60w, the FTIR spectra are almost the same even after water treatment. In plasma polymerization, with the plasma power increasing, the polymer film will become highly branched and cross-linked. The highly cross-linked structure will keep the film insoluble and keep the film attached to the substrate even after the water treatment.

3.1.7 SIMS Spectra Analysis

To confirm the TEM observations shown in Figures 3.2 and 3.3, TOFSIMS was carried out to study the surface films of the particles. Figure 3.12 (a) and (b) show the positive and
negative TOFSIMS spectra of coated ZnO particles. In Figure 3.12 (a) one can see that the spectra of the positive ion from the coated ZnO have strong peaks of functional groups such as C4H7 +, C4H9 +, C6H13O4, C7H9COH +, and C7H9COOH + indicating a surface coating on the particles consistent with the HRTEM data presented in Figures 3.2 and 3.3. In Figure 3.12 (b), where the spectra of the negative ions are presented, we also see the AA monomer, AA dimer, and AA dimer+C2H4 and AA dimer+C3H6, which are strong indications of these functional groups. These are the typical characteristic cluster patterns of a plasma-polymerized poly(acrylic acid) film.

3.1.8 Ion exchange test

In order to investigate the ion remove property, the coated powers have been put into Ni^{2+} solution for 1 hour. After removing the powders, the solution is tested by ion analysis.

Table 3.5: High concentration of Ni solution

<table>
<thead>
<tr>
<th>Test</th>
<th>Condition</th>
<th>Original[Ni] (mg/L)</th>
<th>Final[Ni] (mg/L)</th>
<th>% Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-SIR-700-1</td>
<td>Ion exchange resin</td>
<td>450-500</td>
<td>279</td>
<td>41</td>
</tr>
<tr>
<td>B-PY-1</td>
<td>Monomer: Pyrrole</td>
<td>450-500</td>
<td>416</td>
<td>12</td>
</tr>
<tr>
<td>B-BL-1</td>
<td>Uncoated ZnO</td>
<td>450-500</td>
<td>445</td>
<td>2</td>
</tr>
</tbody>
</table>
### Table 3.6: Medium concentration of Ni solution

<table>
<thead>
<tr>
<th>Test</th>
<th>Condition</th>
<th>Original[Ni] (mg/L)</th>
<th>Final[Ni] (mg/L)</th>
<th>% Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-SIR500-1</td>
<td>Ion exchange resin</td>
<td>102.5</td>
<td>58</td>
<td>43</td>
</tr>
<tr>
<td>B-AA2-1</td>
<td>Monomer: AA; 60wt; 150 mtorr, 2h</td>
<td>114.5</td>
<td>104.5</td>
<td>11</td>
</tr>
<tr>
<td>B-AA3-1</td>
<td>Monomer: AA; 60wt; 300 mtorr, 2h</td>
<td>114.5</td>
<td>104</td>
<td>11</td>
</tr>
<tr>
<td>B-AA17</td>
<td>Monomer: AA; 30wt; 300 mtorr, 2h</td>
<td>104</td>
<td>88.5</td>
<td>15</td>
</tr>
<tr>
<td>B-BL-1</td>
<td>Uncoated ZnO</td>
<td>109</td>
<td>107.9</td>
<td>1</td>
</tr>
</tbody>
</table>

### Table 3.7: Dilute concentration of Ni solution

<table>
<thead>
<tr>
<th>Test</th>
<th>Condition</th>
<th>Original[Ni] (mg/L)</th>
<th>Final[Ni] (mg/L)</th>
<th>% Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-SIR-500</td>
<td>Ion exchange resin</td>
<td>1.15</td>
<td>0.35</td>
<td>70</td>
</tr>
<tr>
<td>B-CG8H</td>
<td>Ion exchange resin</td>
<td>1</td>
<td>0.6</td>
<td>40</td>
</tr>
<tr>
<td>B-AA6</td>
<td>Monomer: AA; 30wt; 200 mtorr, 2h</td>
<td>1.15</td>
<td>0.75</td>
<td>35</td>
</tr>
<tr>
<td>B-AA15</td>
<td>Monomer: AA; 60wt; 300 mtorr, 2h</td>
<td>1</td>
<td>0.45</td>
<td>55</td>
</tr>
<tr>
<td>B-BL-1</td>
<td>Uncoated ZnO</td>
<td>1</td>
<td>1.09</td>
<td>0</td>
</tr>
</tbody>
</table>
From Tables 3.5, 3.6, 3.7, we can see the coated powders really absorb some ions from solution even the result is not as good as resins. But the coated ZnO particles absorb much more ions than uncoated powders. For ion exchange, the most important thing is getting many COOH function groups, because this function group can react with Ni^{2+}. But there is a problem. With the plasma power increasing, the number of function groups will decrease. But using low power, there will not be enough cross-linking to keep the film insoluble. So how to balance the power level is the most important factors to get better results. If we can optimize the processing parameters, we may get much better results. In any case the different ion absorption properties between uncoated and coated particles further proves that the coating exists.

3.2 Design and Construction of the small Vertical RF Plasma System for Nano-particle Treatment

Usually nanoparticles, especially some functional nanoparticles, such as nanotubes, are very expensive. If we still use the common RF system, it will be very expensive and inconvenient. In order to have a special tool to treat nanoparticles, a scaled down RF reactor for plasma treatment of nano-size powders was set up. The reactor was based on the vertically mixing principle and can be used to treat trace amounts of powder.

3.2.1 Principle

As a plasma process can operate in a small parameter-space and due to the complexity of interaction between the parameters, it is important to understand, at least to first approximation, how to adjust the plasma parameters according to changes in the size of the reactor.
The substrate temperature will normally be kept unchanged during the transfer of the process from a common to a small reactor. The main question is how to adjust gas flow rates, pressure, and electrical power in such a way that the scale down of the reactor will not significantly affect the plasma chemistry. For this purpose, plasma processing can be conceptualized as being composed of two subsequent processes:

1. Formation of reactive species
2. Mass transport of the reactive species to the processed surface by convective diffusion

For the first process, it has been theoretically shown that, if dissociation of the precursor molecules takes place through single collisions, the rate coefficients for the reactions caused by electrons depend only on the value of the ratio E/p. (E is electric field strength, p is pressure). One may therefore consider as a first approximation the fact that molecular dissociation rates caused by electron impact are dependent only on the E/p ratio. However, if dissociation is produced through multiple collisions, the dependency on E and p is more complex. It is therefore usually not sufficient to keep only the E/p ratio constant when scaling down the process.

Because the product D.p (D is the diffusion coefficient) is constant for a gas, the mass transport through diffusion is also pressure dependent. Therefore, to preserve both the plasma chemistry and the mass transport during scale down, one has to keep both p and E unchanged during scale down. To maintain the same electrical field strength across the discharge over the smaller area of the manufacturing reactor, it is required to decrease the total current or power supplied to the discharge. In a parallel plate reactor, where the plasma is usually confined between the electrodes, the power has to be scaled linearly with the electrode area to keep the
electric field constant. In other type of reactors, especially in electrodeless ones, the plasma volume does not coincide with the volume between electrodes and is affected by both pressure and flow rate. The power of the scaled down reactor has to be therefore readjusted, often experimentally.

With the electric field, pressure, and substrate temperature kept constant during scale down, the only external adjustable parameter left is the gas flow rate. The average gas flow velocity determines the convective mass transport of the reactive species to the average flow velocity identical in small and large reactors. It can be shown that this requirement regarding the flow velocity scales the gas flow rates proportional to the cross-sectional areas of the reaction zones, perpendicular to the gas flow direction.

A different approach is to keep the same average gas residency time, Tr, in both large and small reactors. The residency time is defined as

\[ \tau_r = \frac{pV_{olr}}{Q} \]

Where \( V_{olr} \) = volume of reaction zone and

\( Q \) = total mass flow rate

The gas residency time is a measure of the average distance over which the reactive species diffusion in the reaction zone, and thus determines the diffusional mass transport. According to the above equation, if the pressure is kept constant, the requirement of constant residence time scales the gas flow rates proportional to the volumes of the reaction zone. If the interelectrode distances are the same in the large and small parallel plate reactors, the
requirements for the same gas velocity and same gas residency time are equivalent. In other types of reactors, the volume of the reaction zone can be dependent on the gas flow rate, and this approach cannot be used.

In summary, the main process parameters that have to be adjusted during scale down to a first approximation as following:

(1) Sample temperature: unchanged
(2) Pressure: unchanged
(3) Electric power: proportional to area of electrodes in parallel plate reactors
(4) Gas flow rates: proportional to electrode area normal to the flow direction or proportional to volume of reaction zone.

3.2.2 Design and Construction

The design of the reactor is shown in Figure 3.13. This reactor consists of a Pyrex cylindrical chamber of 20cm length and 10cm diameter. In the middle of the chamber, there is a convexity circle where samples container can be put on. The plasma is generated through the RF coils with 5-6 turns rolled over the chamber and is maintained by a Radio Frequency energy generator with matching box. The powders are treated in the plasma zone. At the center of the chamber cover, there is an inlet, which can be used to install a shaft to do the mechanical stirring. If the mechanical stirring is not necessary, a glass stopper can be used to close this opening. There are three other inlets on the chamber cover. The three inlets are the same size. These inlets can be used to install the pressure gauge and input monomers. The whole chamber is put on a
magnetic stirrer. Usually magnetic stirring was used to mix the powder, except for some special powders, such as magnetic particles. Small stirring bars mixed with the powders are put into the sample container. In the magnetic field, bars will rotate and vibrate, like a ball mill machine. The powder will be mixed efficiently. The monomers are input from upside (if necessary carrier gas can be used) and pumped down from bottom. The monomer will be active in the plasma zone, and then reach the particles in the container. A filter is a very important part in this reactor. An effective separation of the fine particles and the gas flow to the pump has been a major stumbling block in the development of plasma processes for powders. Particles are collected on the filter, which has to be cleaned or replaced after each run.

All the monomers or carrier gas are controlled by the mass flow controller (model 2259B from MKS instruments, Inc). This controller will be calibrated for other gases and a number of vapors. The equation used to calibrate is following:

\[
GCF = \frac{0.3106(a_1s_1+a_2s_2+...+a_ns_n)}{a_1d_1c_{p1}+a_2d_2c_{p2}+...+a_nd_nc_{pn}}
\]

Here, \(a_1\) through \(a_n\) are the fractional flows of gas 1 through n; \(s_1\) through \(s_n\) are molecular structure factors; \(d_1\) through \(d_n\) are the standard densities; \(c_{p1}\) through \(c_{pn}\) are the specific temperatures. Values for \(s,\ d\) and \(c\) are available for most gases and can be got from manual.

The pressure gauge used here is a thermocouple pressure gauge. The thermocouple gauge is a “thermal conductivity-type” gauge. It measures the cooling effect that the residual gas has on a heated thermocouple within the molecular flow regime. The pressure range of utility is typically from 1 mtorr to 1 torr. In order to measure the pressure below 1 mtorr (when we need to
use the diffusion pump), the thermocouple gauge is used in conjunction with the ionization
gauge to cover the pressure range from $10^{-11}$ to 1 torr. The principle of operation of the ionization
gauge is that residual gas particles are ionized and an ion current is measured. The ion current is
proportional to the ion density, which is proportional to the neutral particle density, which, is
proportional to the pressure.

Strong radio waves are harmful to people and the environment. For safety purposes, metal
mesh outside of the chamber is set up to protect people who operate the system and to shield the
radio waves.

Since in all plasma polymer deposition experiments the substrate has to be thoroughly
cleaned and activated before deposition, this reactor design allows such a step by first treating
the particles in a plasma of argon. After cleaning processing, argon will be shut down and the
monomer vapor will be introduced at a steady flow rate. The powders are then coated within the
plasma of the depositing monomer.

3.3 Plasma Coating of Nanomaterials

In order to investigate the new plasma system, several coating experiments have been
performed on this small system.

3.3.1 Plasma Coating of Magnetic Nanoparticles
Table 3.8: Process parameters for RF-plasma coating of a polymer on magnetic nanoparticles

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma Power (W)</td>
<td>5-30</td>
</tr>
<tr>
<td>Base pressure, (mTorr)</td>
<td>30-50 mTorr</td>
</tr>
<tr>
<td>Total gas pressure, (mTorr)</td>
<td>100 – 300 mTorr</td>
</tr>
<tr>
<td>Monomer/Precursor Gas</td>
<td>Styrene</td>
</tr>
<tr>
<td>Deposition duration</td>
<td>1min-30min</td>
</tr>
<tr>
<td>Deposition Temperature</td>
<td>Ambiance</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>Powder/particle size</td>
<td>NiFe$_2$O$_4$</td>
</tr>
<tr>
<td>Polymer coating thickness</td>
<td>2-10 nm</td>
</tr>
<tr>
<td>Stirring method</td>
<td>Mechanical Stirring</td>
</tr>
</tbody>
</table>

3.3.1.1 Microstructure of the Coated Powder

In Figure 3.15, there is a bright ring outside the particle, which did not appear in Figure 3.14. In the high-resolution picture, the coating layer is amorphous compared with the lattice structure from the substrate particles. But from the images of the original particles (Figure 3.14), we do not see this amorphous layer. Thus, we are certain that the observed layer is due to coating rather than an artifact in the TEM observation.

From Figure 3.15, we can see the magnetic particle aggregated together, the coating is only on the outside of the cluster not exactly on the surface of each particle. But the impurity particles like TiOx and Cu (Figure 3.16) have a very uniform coating on individual each particle. We can reach this conclusion: the mechanical stirring is satisfied for regular nanoparticles, but
not for the magnetic particles, because the natural magnetic properties of NiFe$_2$O$_4$ make it much more difficult to mix.

3.3.1.2 EDS Analysis

Typical EDS spectra of coated and uncoated samples are shown in Figure 3.17 (a) and Figure 3.17 (b). After the plasma coating, the peak of Fe and Ni decreases and the carbon peak increases sharply, indicating the outside layer has different compounds as compared with the NiFe$_2$O$_4$ particle. This observation further proves the outside is a new layer rather than an artifact in the TEM observation. In the spectrum, some Cu peaks can be found. These elements are impurities.

3.1.3 FTIR Spectra Analysis

Table 3. 9: *Peak assignment for Polystyrene films of Figure 3.18*

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3027</td>
<td>Asymmetric and symmetric C-H stretching vibration of saturated hydrocarbons</td>
</tr>
<tr>
<td>2931</td>
<td></td>
</tr>
<tr>
<td>1601</td>
<td>The vibrating absorption of C-C on benzene ring</td>
</tr>
<tr>
<td>1494</td>
<td></td>
</tr>
<tr>
<td>1452</td>
<td></td>
</tr>
<tr>
<td>758</td>
<td>C-H out of plane bending. Two peaks mean one H substituted by other function group. The structure is:</td>
</tr>
<tr>
<td>700</td>
<td></td>
</tr>
</tbody>
</table>
In Figure 3.18, the spectrum exhibits several very strong peaks between 1400 cm\(^{-1}\) and 1600 cm\(^{-1}\), which is due to the C-C vibrating absorption of the benzene ring. These peaks are the special absorption of the benzene ring. These peaks confirm the plasma polymer structure contains some benzene rings. In the FTIR absorption spectrum, the range from 690 cm\(^{-1}\) to 900 cm\(^{-1}\) belongs to the benzene C-H out of plane bending. The relationship between the substituted position and the number of peaks is shown in Table 3.10:

**Table 3.10: Benzene C-H out of plane bending absorption**

<table>
<thead>
<tr>
<th>The position of substituted function group</th>
<th>The number of peak</th>
<th>Frequency/cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td>2</td>
<td>730-770</td>
</tr>
<tr>
<td><img src="image2.png" alt="Image" /></td>
<td>1</td>
<td>735-770</td>
</tr>
<tr>
<td><img src="image3.png" alt="Image" /></td>
<td>3</td>
<td>860-900</td>
</tr>
<tr>
<td><img src="image4.png" alt="Image" /></td>
<td>1</td>
<td>800-860</td>
</tr>
<tr>
<td><img src="image5.png" alt="Image" /></td>
<td></td>
<td>680-725</td>
</tr>
<tr>
<td><img src="image6.png" alt="Image" /></td>
<td></td>
<td>750-810</td>
</tr>
</tbody>
</table>
From table 3.10, only when the function group substitutes one hydrogen atom on the benzene ring, there are two peaks on the FTIR spectrum. Actually on Figure 3.18, at 758 cm$^{-1}$ and 700 cm$^{-1}$ there are two peaks, which is the special absorption for one substituted.

### 3.3.2 Co-polymer Coating of YYbErO$_2$S

The particle used here is one kind of luminescent particle. This particle will be used as the substrate for bacteria detection. The outside coating needs to contain the C=O function group which can be used to attract the bacteria. But the concentration needs to be controlled for different conditions. In order to get the C=O function group and control the concentration, two kinds of monomers are used in this coating processing. One is MMA, which used to introduce the C=O function group. Another one is styrene, which is used to control the concentration of C=O. Table 3.11 shows the parameters of this coating processing.

**Table 3.11: Processing parameters of RF-plasma co-polymer coating on YYbErO$_2$S**

<table>
<thead>
<tr>
<th>Plasma Power (W)</th>
<th>5-30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure, (mTorr)</td>
<td>30-50 mTorr</td>
</tr>
<tr>
<td>Total gas pressure, (mTorr)</td>
<td>200 – 300 mTorr</td>
</tr>
<tr>
<td>Monomer/Precursor Gas</td>
<td>Styrene/MMA</td>
</tr>
<tr>
<td>Deposition duration</td>
<td>1min-30min</td>
</tr>
<tr>
<td>Deposition Temperature</td>
<td>Ambiance</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>Powder/particle size</td>
<td>YYbErO$_2$S (300 nm)</td>
</tr>
<tr>
<td>Polymer coating thickness</td>
<td>10-15 nm</td>
</tr>
<tr>
<td>Stirring method</td>
<td>Magnetic Stirring</td>
</tr>
</tbody>
</table>
3.3.2.1 Microstructure of the Coated Powder

Figure 3.19 is the HRTEM image of the coated particle. In Figure 3.19, there is a bright ring on the particle surfaces, which is the result of the polymer coating. Figure 3.19 has the high magnification images showing a uniform coating on the particle surfaces. The coating thickness is approximately 10nm over the entire particle surface. The coating layer is amorphous based on the HRTEMs of different particles.

3.3.2.2 EDS Analysis

From Figure 3.20 and Figure 3.21, we can see that the uncoated spectrum has very strong Y and Eu peaks. But in the coated spectrum, almost all of these peaks become weak. And a new strong peak appears, the C peak. This peak comes from coating polymer.

3.1.3 FTIR spectra analysis

In Figure 3.22, Figure 3.23, and Figure 3.24, there are several strong peaks belonging to different function groups. The peak around 1700 cm\(^{-1}\) is the special absorption of C=O vibration. The peaks between 1450 cm\(^{-1}\) and 1700 cm\(^{-1}\) belong to the C-C vibration of the benzene ring. The molecular structure of the monomers styrene and Methyl methacrylate (MMA) are:
Table 3.12: Peak assignments for the polymer films from the styrene and MMA co-polymerization of Figure 3.24, 3.25, 3.26

<table>
<thead>
<tr>
<th>Frequency cm(^{-1})</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1720</td>
<td>C=O stretching vibration</td>
</tr>
<tr>
<td>1601</td>
<td></td>
</tr>
<tr>
<td>1494</td>
<td>The vibrating absorption of C-C on benzene ring</td>
</tr>
<tr>
<td>1452</td>
<td></td>
</tr>
<tr>
<td>760, 700</td>
<td>C-H out of plane bending. Two peaks mean one H substituted by other function group. The structure is:</td>
</tr>
</tbody>
</table>

From the molecular structure of the monomer, we can see that the benzene ring comes from styrene and the C=O function group comes from the MMA. Comparing Figures 3.22, 3.23, and 3.24, the intensity of the peaks between 1450-1600 cm\(^{-1}\) and the peaks around 700 cm\(^{-1}\) and
760 cm\(^{-1}\) decreased with the ratio of styrene/MMA decreasing, the intensity of peaks changing means the concentration of different function group has changed. With the MMA concentration increasing, the peak around 1700 cm\(^{-1}\) becomes stronger and stronger. This evidence means more MMA monomer is used in plasma coating, more C=O function groups occur in the coating films. The FTIR data strongly prove through controlling the ratio of monomer, the molecular structure of the coating polymer can be modified as desired.

### 3.3.3 Plasma Coating of Multi-Wall Carbon Nanotube

<table>
<thead>
<tr>
<th>Process parameters of the RF-plasma polymer coating on MWCNT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Plasma Power (W)</strong></td>
</tr>
<tr>
<td><strong>Base pressure, (mTorr)</strong></td>
</tr>
<tr>
<td><strong>Total gas pressure, (mTorr)</strong></td>
</tr>
<tr>
<td><strong>Monomer/Precursor Gas</strong></td>
</tr>
<tr>
<td><strong>Deposition duration</strong></td>
</tr>
<tr>
<td><strong>Deposition Temperature</strong></td>
</tr>
<tr>
<td><strong>Substrate Temperature</strong></td>
</tr>
<tr>
<td><strong>Powder/particle size</strong></td>
</tr>
<tr>
<td><strong>Polymer coating thickness</strong></td>
</tr>
<tr>
<td><strong>Stirring method</strong></td>
</tr>
</tbody>
</table>
The nanotubes are stirred in the sample container at the middle of the chamber and thus the surface of the particles can be continuously renewed and exposed to the plasma for thin film deposition during the plasma polymerization process. Two small magnetic bars were used to stir the powders. Because the density of the NT is small, a mesh cover was used to prove the MWNT spray out off the sample container during the virogsously stirring. Before the plasma coating, the argon gas was introduced from the inlet and the plasma generator was turned on at 60w, which is higher than the power used for plasma coating. This processing will clean the surface of the particles. After 30 minutes ion bombardment, styrene and C_6F_{14} gas with controlled ratio were introduced from another gas inlet at the same time as the argon gas was shut down. The operating pressure was adjusted by the gas/monomer mass flow rate. The total pressure was about 350 mTorr. During the plasma polymerization process, the input power was 15 W. The plasma treatment time was 10 minutes. Per batch, 0.1 grams of powder were treated.

After the plasma treatment, the MWCNTs were examined using TEM, and TOFSIMS. HRTEM experiments were performed on a JEOL JEM 4000EX TEM.

### 3.3.3.1 Microstructure of Coated Powder

Figure 3.25 shows the bright-field TEM images of the original, uncoated Pyrograf III PR-24 carbon nanotubes (Figure 3.25). As can be seen in this figure, the carbon nanotubes have similar features in dimension with a hollow channel. The Pyrograf III PR-24 nanotubes have the outside diameters averaging about 70 nm and quite uniformly distributed. Some nanotubes become curved during their growth with the open ends. HRTEM image (Figure 3.26 (A)) of the original Pyrograf III PR-24 carbon nanotubes shows the graphite structure with the interlayer
spacing $d_{002}=0.34$ nm. Based on the bright-field TEM and HREM images, the wall thickness of the nanotubes can be estimated to be about 20~30 nm. Nanotubes with axially parallel graphite layers (not shown here) and the nanotubes with axially parallel graphite layers oriented at an angle to the tube axis (Figure 3. 26 (A)) are observed. The edge dislocations can be seen due to the disorder of the graphite layers (002). It is noticed that both outer and inner surfaces terminate at graphite (002) layer without an addition of surface layer for originally uncoated nanotubes (Figure 3. 26 (A)). The bright field and high-resolution TEM images of these nanotubes after plasma treatment are shown in Figure 3. 26 (B) and Figure 3.27, respectively. An ultrathin thin film of amorphous layer can be clearly seen over the surfaces of the Pyrograf III PR-24 nanotubes (Figure 3.26 (B)). The thin film is uniform on the surfaces of MWNT. (Figure 3.26 (B)). The thickness of ultrathin film is approximately 2~7 nm all the way surrounding the nanotube surfaces for Pyrograf III PR-24 carbon nanotubes that is thicker and more uniform than the disturbance (<1 nm) on the outer surface of carbon nanotubes (Figure 3.26 (A)). This coating can only be attributed to be remarkably uniform layer of coating. In Fig 3.27(B), we show the HRTEM image of a coated Pyrograf III PR-24 carbon nanotube. The lattice image of graphite can be clearly seen with an extremely thin layer of polymer film on its surface.

### 3.3.3.2 SIMS Spectra Analysis

To confirm the TEM observations shown in Figure 3.26, 3.27, TOFSIMS was carried out to study the surface films of the MWNT. Figure 3. 28 and Figure 3.29 shows the positive TOFSIMS spectra of coated and uncoated MWNT. In Figure 3.28, one can see that the spectra of the positive ion from the uncoated MWNT have strong peaks of functional groups such as $C_1$, $C_2$, $C_3$, $C_4$, $C_7H^+$ and $C_{10}H_8^+$ indicating the surface of MWNT contains hydrocarbon. Because
the plasma coating of polystyrene only contain Carbon and Hydrogen, the hydrocarbon from the surface of MWNT will cause the problem to identify the coating from the MWNT surface. In order to solve this problem, a little bit C6F14 was added to co-polymerize with styrene monomer. In Figure 3.31, one can see that the spectrum of the positive ion from coated MWNT have strong peaks such as CF+, C2F+, C4F6+, C3F7+, C4F7+, C5F7+ indicating Fluorine in the coating film. The fluorine only can came from the monomer, which strongly prove the existence of coated film
Chapter 4: DISCUSSION AND CONCLUSIONS

In summary, a thin polymer film of pyrrole and acrylic acid has been deposited on the surface of Zinc Oxide particles by a plasma polymerization treatment. The polymer layer is a uniform coating on irregularly shaped ZnO particles with an average thickness of 5 nm. SIMS studies verify the polymer coating and indicate the cross-linked polymer pattern.

TOFSIMS experimental results have confirmed the deposited film to be a polyacrylic acid polymer. The effect of plasma power on the structure of the polyacrylic film has been studied by FTIR experiments. The plasma power dependence indicates that the cross-links are enhanced at higher powers. The coating film changes from soluble to insoluble with the power increasing.

The ion exchange experiments further prove that the surface property of the nanoparticles have been changed by the plasma processing. The functional groups, introduced by plasma processing, give the nanoparticles an ion absorption property and give the nanoparticle much wider useful areas.

In other coating researching, ultrathin polymer film(s) have been deposited on the surface of several kinds of nanoparticles such as: NiFe$_2$O$_4$, YYbErO$_2$S and carbon nanotube Pyrograf-III PR-24 by plasma treatment. The polymer layer is not only uniform on all particle sizes, but also deposited in an extremely thin thickness, 2-10 nm. HRTEM and TOFSIMS studies verify the polymer coating and IR indicates the structure of the polymer coating on the surface of particles. Furthermore, the unique nanostructures obtained in this study provide great opportunities for
research in fundamental sciences that will be profoundly important in many related fields such as electronic devices, bioengineering, and materials science.
Nanotechnology has been the most important research topic in the world for the past few years and will change our lives in the near future. How to use nanoparticles and how to modify the surface of nanoparticles is an important component of nanotechnology research.

Major challenges must be faced before use of the modified nanoparticles becomes a commonplace reality. First, is how to find a more efficient stirring method to improve the reproduction of the coating for each patch. In plasma processing, if the substrate is flat or two dimensions, controlling the plasma processing parameters will give good control of the film properties, including the thickness and the composition. This technique has been widely used in the semi-conductive industry for wafer modification. But for nanoparticles or one-dimension substrate, the stirring methods play a very important role in the whole processing. The methods we used here are magnetic stirring and mechanical stirring. This parameters are difficult to control, which affects the reproduction of the coatings. In the future, an efficient way to stir the powder will be a key to move plasma technique to industry.

For further development of the plasma surface coating technique, it is suggested that different monomers be employed for the coating. Different experimental conditions also need to be tried in order to get a uniform film on the nano surfaces. Although polymers have been used wildly in plasma treatment, metals or conducting materials can also be used to coat to explore how the electrical conductivity of the coated nano particles changes.
Figure 1.1: Schematic representation of the step growth mechanism of Plasma polymerization
Figure 1.2: Diagram of plasma polymerization. Solid line, polymer deposition path; broken line, volatile product formation path.
Figure 1.3: Diagram of a DC reactor
Figure 1.4: Diagram of a RF reactor
Figure 1.5: Schematic of stirred plasma reactor for powders
Figure 1.6: Diagram of a microwave power system for cold plasma excitation
Figure 1.7: Distribution of film thickness along the gas flow.

The total active discharge duration was 20s.
Figure 1.8: Cross-sectional AFM images of (a) a Si substrate and (b) a thin organic film on Si
Figure 3.1: The plasma reactor for thin film coating of the nano-particles; a) Schematic diagram, b) Fluidized bed reactor.
Figure 3.2: TEM image of uncoated ZnO at different resolutions
Figure 3.3: TEM image of Poly (acrylic acid) coated ZnO particles at different resolutions
Figure 3.4: TEM image of PPy Coated ZnO particles at different resolutions
Figure 3.5: EDS analysis of a) uncoated and b) AA coated powder
Figure 3.6: FTIR spectrum of the Pyrrole monomer
Figure 3.7: FTIR spectra of the RF Poly-Pyrrole
Figure 3.8: FTIR spectra of poly-(acrylic acid) film (power 60w)
Figure 3.9: FTIR spectra of poly (acrylic acid) at different power levels
Figure 3.10: Contact angle of polymer film versus plasma power
Figure 3.11: FTIR of the plasma film before and after water treatment
Mass, amu

(a) Positive image
Figure 3.12: SIMS spectra of coated samples (a) Positive image

(b) Negative image
Figure 3.13: The Schematic diagram of the new plasma reactor
Figure 3.14: TEM image of uncoated NiFe₂O₄ at different resolutions
Figure 3.15: TEM image of coated NiFe₂O₄ at different resolutions
Figure 3.16: TEM image of coated impurity TiOx in magnetic particles at different resolutions
Figure 3.17: EDS spectrum of coated and uncoated magnetic particles
Figure 3.18: FTIR spectra of RF Polystyrene
Figure 3.19: TEM image of coated YYbErO$_2$S at different resolutions
**Figure 3.20:** EDS spectrum of uncoated particles
Figure 3.21: EDS spectrum of coated particles
Figure 3.22: FTIR of the coated particle (condition: Styrene 200mtorr, MMA 50mtorr)
Figure 3.23: FTIR of the coated particles (condition: styrene 150mtorr, MMA 100mtorr)
Figure 3.24: FTIR of the coated particles (condition: styrene 100mtorr, MMA 150mtorr)
Figure 3.25: Bright-field TEM images of the original, uncoated carbon nanotubes
Figure 3.26: HRTEM images of nanotubes: (A) The fragments of the wall with inclined planes (002) showing lattice space on the outer and inner surfaces of uncoated nanotubes with slight disturbance (<1 nm) on the surface; (B) An ultrathin film can be observed on the surface of coated nanotubes.
Figure 3. 27: The bright-field TEM (A) and HRTEM images (B) showing the coating on the surface of the nanotube. The lattice image of carbon can be clearly seen with an extremely thin layer of polymer film (~2 nm) on the outer surface of the coated Pyrograf III PR-24 carbon nanotube.
**Figure 3.28:** Positive SIMS spectrum of uncoated MWCNT
Figure 3.29: Positive SIMS spectrum of coated MWCNT


