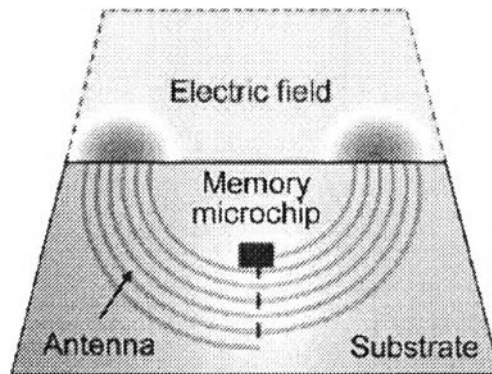# CHAPTER II

LITERATURE REVIEW

2.1 Sensor

Battery-free radio frequency identification (RFID) sensors for food quality and safety were investigated by Potyrailo et al. (2012). They found that the electric field generated in RFID sensor antenna which had sensing films deposited on it by food changed pH or quality led to changed conductivity and electricity.


Figure 2.1 The electric field generated in RFID sensor antenna extends from the plane of RFID sensor.
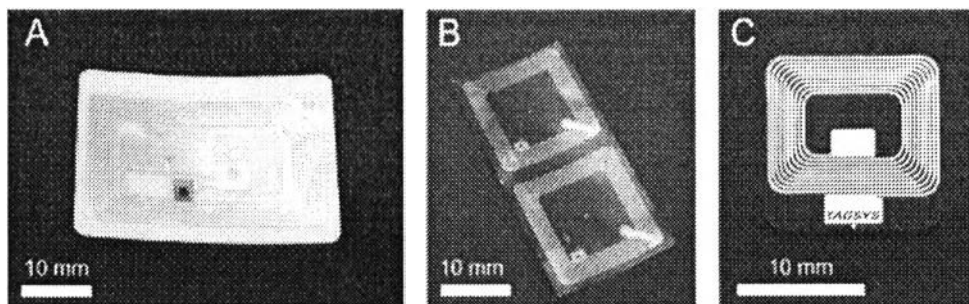

Figure 2.2 Examples of employed RFID sensors based on (A) Texas Instruments, (B) Avery Dennison, and (C) TagSys RFID tag.

For example, sensor attached at the side wall of milk carton could detect milk spoilage changing the ionic content and conductivity of milk following figure 2.3. Program would show green result and become red when milk started spoiling to value that automatic program determination set up for food safety and human health. Fish spoilage, volatiles contributing to the odor off newly caught fresh fish originate from the diverse microflora and include C6-C9 alcohols and carbonyl compounds, whereas volatiles that contribute to the odor of fish during spoilage include ethanol, trimethylamine, ammonia, hydrogen sulfide and some others that were results of microbial spoilage. Volatiles responsible for the fishy odor were the result of bacterial metabolism and include ammonia and volatile amines known as total volatile basic nitrogen compound. Sensor would be attached on the wrap of food container to link with program and detect conductivity or electricity changed by food.
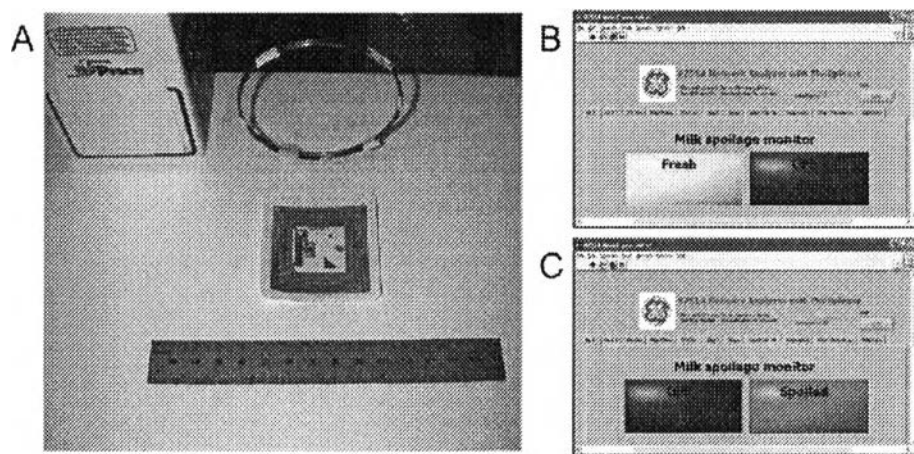
Figure 2.3 (A) a milk carton with an attached RFID sensor, (B) and (C) front panel of written program for automatic determination of the resonant properties of the sensor s without the positioning effects of sensors relative to the pick-up coil.
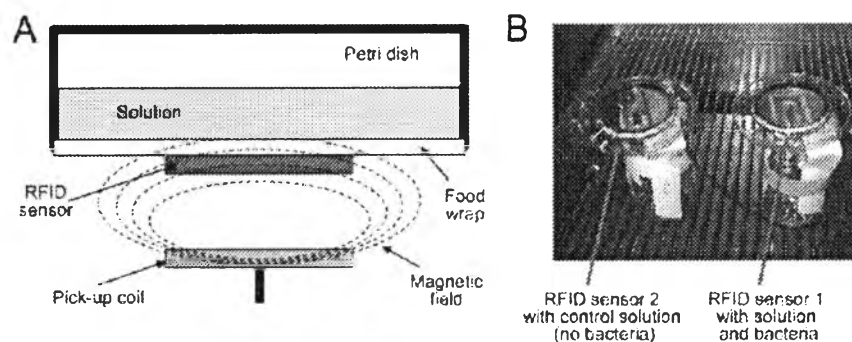
Figure 2.4 RFID sensor layout for demonstration of monitoring of fish freshness: (A) schematic of sensor positioning into the headspace of a plastic container with a fish sample and sensor-response readout with a pick-up coil; (B) photograph of RFID sensors attached to plastic container with fish samples.

2.2 Layer-by-layer Self-assembly

Layer-by-layer assembly is an interesting technique to make the films because it is a simple procedure, does not require any organic solvent, used only small amount of chemical and used electrostatic interaction of macromolecules. For example, substrate was anionic, first chemical adsorption was cationic, second was anionic and repeated this until number of layer was required. It meant using alternated sequential of opposite charge to make the film.

Decher and Hong (1991) investigated the sequential adsorption of anionic and cationic from aqueous solutions. They found this method could be extended to use synthetic polyelectrolyte, DNA, proteins, clay platelets, inorganic or metal colloids, etc. So it enables to construct hybrid films consisting of different material. The build-up of multilayer assemblies by consecutive adsorption of anionic and cationic polyelectrolytes (cyclic repetition of step 1 to 4) following figure 2.5. Top part of figure showed the oversimplified view of how one might envision the charge reversal of the surface of the substrate on the molecular level and bottom part of figure showed the build-up of multilayer films as it was being carried out by using regular beakers. It was not implied that the symbols used for the polyelectrolytes represent their actual structure in solution or after the adsorption. Then Decher *et al.*

(1998) investigated structure on multilayer composed of strong flexible polyelectrolytes, they found that single layer film of high flexibility of polymer like poly(allylamine hydrochloride) (PAH) or poly(styrene sulfonic acid) (PSS) had more roughness than multilayer film due to surface of single layer would be collapsed in dry state but the smoothness increased with number of layer because some polymer newly adsorbed layer penetrated into internal interface, trapped and became swollen so it made surface smoother.
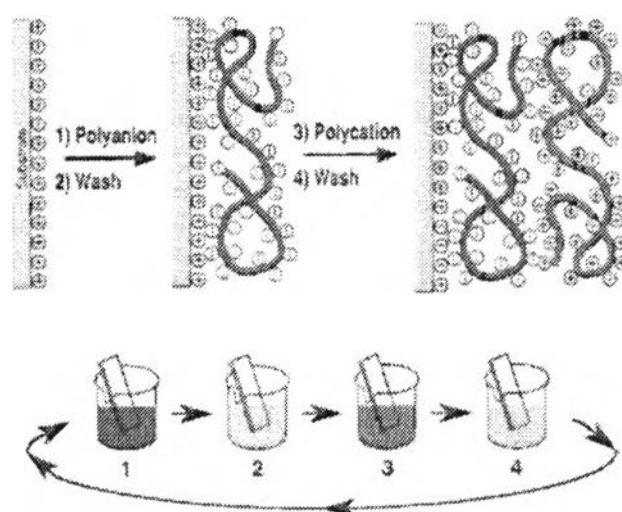

Figure 2.5 Schematic for the build-up of multilayer assemblies by consecutive adsorption of anionic and cationic polyelectrolytes (cyclic repetition of step 1 to 4).

2.3 Conducting Polymer

Conductive polymers or intrinsically conducting polymers (ICPs) are organic polymers, such as polyacetylene, polypyrrole, and polyaniline which are the main class of conductive polymers, and conduct electricity. They can offer high electrical properties that can be fine-tuned using the methods of organic synthesis. Such compounds may have metallic conductivity. Conducting polymers has variety of applications such as organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, chemical sensors and biosensors.

Among conductive polymers, PANI has gained more attention conductive polymer because of its unique properties such as low cost monomer, ease of synthesis, good redox properties, tunable properties, high environmental stability, substantial thermal stability, electrical conductive stability, ability to retard corrosion and numerous application possibilities such as batteries, capacitors, electrochromic windows and displays, actuators, photovoltaic cells, and light-emitting electrochemical cells but the limitation is insoluble in nonpolar solvent.
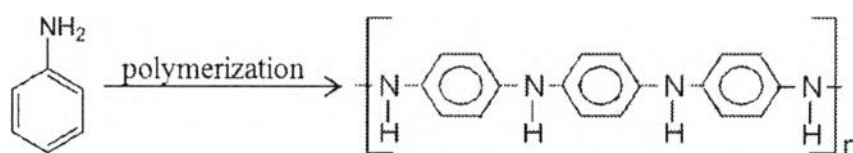
Figure 2.6 Polyaniline polymerization

2.3.1 Polyaniline

Hush (2003) and Inzelt (2008) reported the PANI was first described in the mid-19th century by Henry Letheby, who investigated the electrochemical and chemical oxidation products of aniline in acidic media. He noted that reduced form was colorless but the oxidized forms were deep blue.

There were many techniques or method to polymerize polyaniline such as wet spinning, redox, atom transfer radical (ATRP), redox, electrochemical, chemical oxidative, in situ polymerization even polymerize based on temperature etc.

2.3.1.1 Wet Spinning Polymerization

Polyaniline fiber could prepare in coagulation bath well-known as wet spinning method but this method had toxic organic solvent in coagulation. The long or short fiber got from different coagulation solvent. Zhang *et al.* (2006) investigated wet spinning of pre-doped polyaniline into an aqueous solution of a polyelectrolyte. The length, thickness and fiber shape could get by vary chemical coagulation bath; inorganic salt, small cationic molecules, polycations, and small anionic molecules. They found that spun with small cationic molecules would give poor quality fibers for example propylamine, and hexadecyltrimethylammonium bromide, spun with polycations would give longer fiber but still low quality such as

poly(allylaminne hydrochloride) (PAH) and poly(diallyldimethylammonium chloride) (PDADMAC). They got the longest fibers of the aqueous solutions when they spun into poly(styrene sulfonate acid) sodium salt (PSS) and poly(methacrylic aicd) based on conjugate of strong and weak acid group, respectively because they could absorb onto the PANI surface by electrostatic interaction and stabilize it. Moreover, they found that length of fibers and smoothness increased with concentration of PSS. The conductivity of fibers with vary concentration of PSS was highest at 5% PSS concentration of their experiment.

### 2.3.1.2 Atom Transfer Radical Polymerization

Chu et al. (2005) synthesized conductive star polymers nanocomposite containing PSS/PANI arms. They prepared star polymer by first, polystyrene was prepared then use it to make star shape with atom transfer polymerization and introduce sulfonated group, and eventually, polyaniline was synthesized at that group. They found that star PSS/PANI was highly stable in aqueous solution and excellent solubility in water due to poly(styrenesulfonated) used as steric stabilizer and codopant.
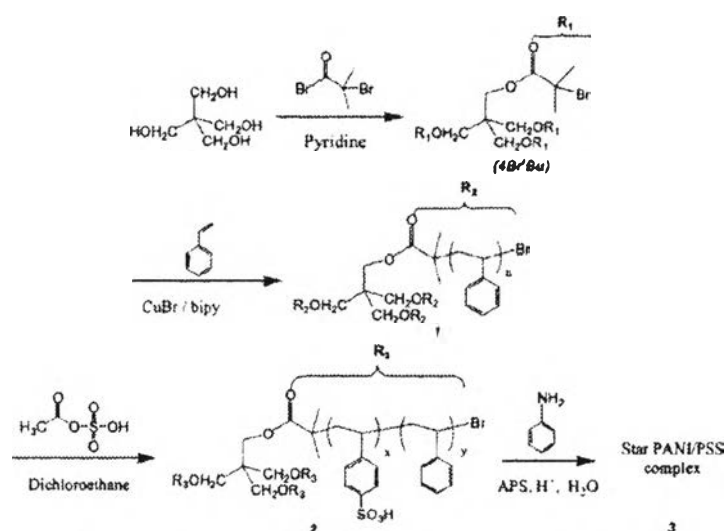
Figure 2.7 Synthesis of 4-armed starburst polyaniline/poly(styrenesulfonate) complex.

2.3.1.3 Redox Polymerization

Structure and mechanical properties of pure and doped polyaniline were investigated by Shaktawat et al. (2011). They were synthesized polyaniline by redox polymerization. Aniline dissolved in hydrochloric acid, stirred and added dropwise diammonuim persulfate (APS) at 0°C for 2 hours and then kept the solution for 24 hours. They found that doped polyaniline with acid could enhance electrical conductivity, mechanical flexibility, stability and process properties because it had more dense, compact and order structure than pure polyaniline. Moreover, PANI could change the structure after doping, electrical mechanical and optical properties would change also following figure 2.8. It showed that (a) was polyaniline before doping in acid, (b) was polyaniline first step doped "bipolaron" but it was not stable so led to more stable in "polaron" form (c).
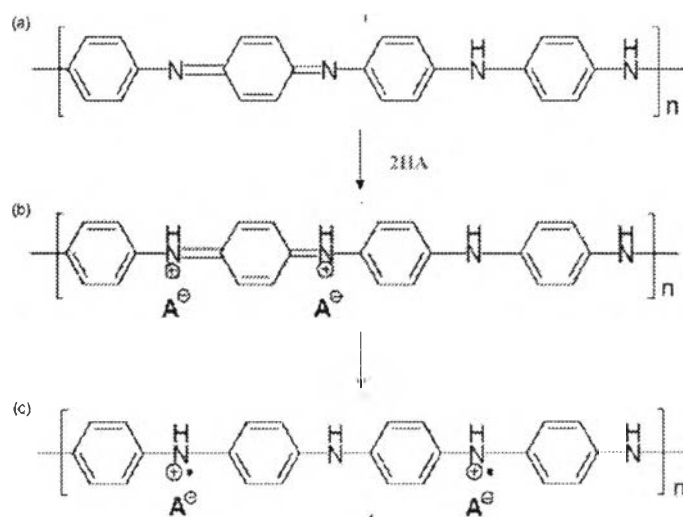
Figure 2.8 Principal of PANI doping: (a) emeraldine base, (b) intermediate dicationic species, and (c) emeraldine salt.

They found that both pure and doped polyaniline had modulus decrease from 50°C to 150°C changed amorphous state to rubbery state because warm made material expanded and moved bond and side chain after 150°C was

permanent change. The phase transition had shift to higher temperature after doped because dopant size made structure more compact or less void.

2.3.1.4 Electrochemical

Wang and Levon (2012) polymerized polyaniline (PANI) with various doping agent by electrochemical method. Polyaniline was polymerized on glass carbon (GC) electrode which was hydrophobic then applied voltage to initiate and growth polyaniline on it (overall cycle was 60). PANI on GC electrode was rinsed in water, dipped polyelectrolyte solution and altered this method three times to make multilayer films. PANI on GC electrode was applied voltage with pH solution to observe sensitivity. They found that PANI doped with sulfuric acid on GC electrode had degradation peak at 500V due to oxidation of the film. PANI within range of potential polymerization between -150V and 850V had higher growth rate and more risk of polymer degradation which led to less conducting PANI films than range between -200V and 900V for initiation PANI on surface and decrease to -150V and 780V for film growth. They investigated effect of dopant on pH sensitivity of PANI because PANI by itself had pH lower than 3 and no conductivity, they found that hydrophilic structure of dopant could polymerize faster than hydrophobic structure and the fastest polymerization as dopant could release two proton such as sulfuric acid. Effect of polyelectrolyte, strong polyelectrolyte acid macromolecule could compensate all cationic sites on PANI enough and form complex to increase sensitivity of pH and stability of films especially polystyrene sulfonic acid.

2.3.1.5 Chemical Oxidative Polymerization

Normally, Solubility polyaniline could increase by either doping with a suitable dopant or modify starting monomer. Doping with suitable dopant made solubility and conductivity increased. Modify starting monomer, substituted polyaniline made solubility increased but conductivity decreased from 10^{-4}-10^{-7} s/cm because steric hindrance made polyaniline lost planarity. Bhadra et al. (2010) synthesized water soluble sulfonated polyaniline by using chemical oxidative polymerization based on the incorporation of an aromatic substitution in polyaniline. First, they prepared polyaniline (PANI) in order to synthesize water soluble sulfonate polyaniline (SPANI). PANI was investigated good yield and conductivity by using ratio of three chemicals; aniline monomer: hydrochloric acid: ammonium persulfate

used as oxidizing agent is 1: 0.1: 1.This step took time around 5 days to get it. Water soluble SPANI was synthesized by use PANI fumed in sulfuric acid. This step took time around 5 days also. They showed results that PANI had three basic structures pernigraniline base (PNB), leucoemeraldine base (LEB) and Emeraldine base (EB) following figure 2.9. PNB and LED were insulating form even after doped. EB had high concentration in PANI and SPANI so they could be conductive polymer. Conductivity of PANI (0.073 s/cm) had higher than SPANI (0.031 s/cm). Conductivity of SPANI decreased due to its structure had more bipolaron through extra protonation and electron density decrease at polymer backbone. This method could get 94% sulfonation degree of SPANI and solubility was 1.25 g/l or more hydrophilic than PANI because of sulfonation of aromatic ring. Moreover, SPANI had higher thermal stability, size and molecular weight because of sulfonic acid group.
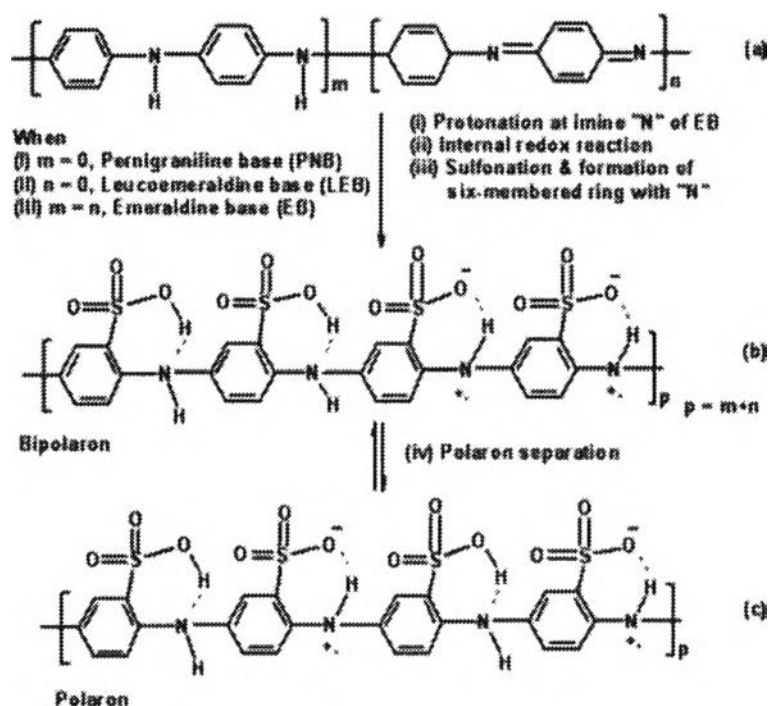
Figure 2.9 (a) Different structures of polyaniline based on oxidation levels: (I) fully oxidized pernigraniline base (PNB), (II) fully reduced leucoemeraldine base (LEB) and (III) half oxidized emeraldine base (EB). (b) Bipolaron formation after
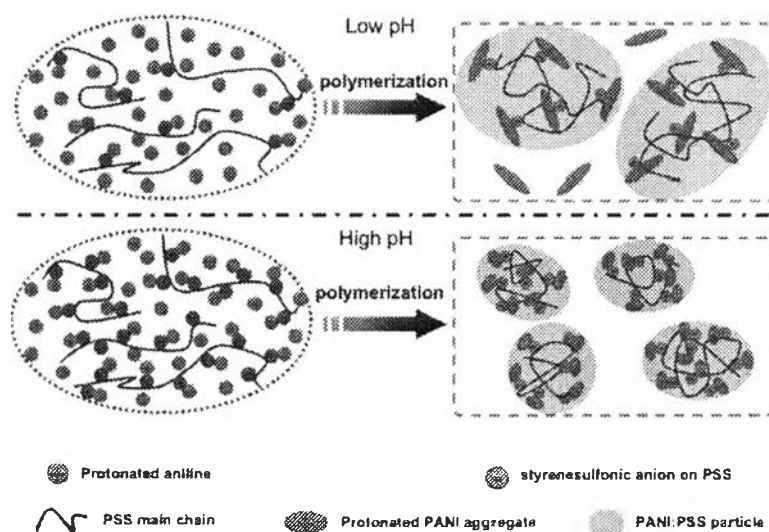
protonation of EB, sulfonation of polyaniline and formation of six-membered self-doped ring structure. (c) Bipolaron to polaron transition.

Polyaniline coated polystyrene-poly(styrene-co-sodium 4-styrenesulfonate) microparticles and further fabrication of hollow polyaniline microspheres were prepared and investigated by Sun *et al.* (2011).There were four steps including preparation monodispersed PS, PS-PSS, polymerization PANI on core of PS-PSS following figure 2.10 and PS-PSS was dissolved with chloroform to get hollow PANI microspheres, respectively. They found that PS was highly monodispresed, spherical shape and smooth surface. PS-PSS became hard uniformly dispersed when amount of sodium 4-styrenesulfonate (SSS) was high because long chain SSS was probably winding with each other. (PS-PSS)/PANI, sulfonic group of PSS could enhance interaction between core and shell with strong electrostatic attraction and improve stability and conductivity of composite particles. (PS-PSS)/PANI would have uniform surface when amount of aniline had enough and could wrapped around the core. Hollow PANI microsphere, morphology would keep uniformly spherical shape when PANI could connect in all place and thick enough. Conductivity of (PS-PSS)/PANI was increase with coating PANI because of connection of conducting polymer while hollow PANI had conductivity quite same the pure PANI.
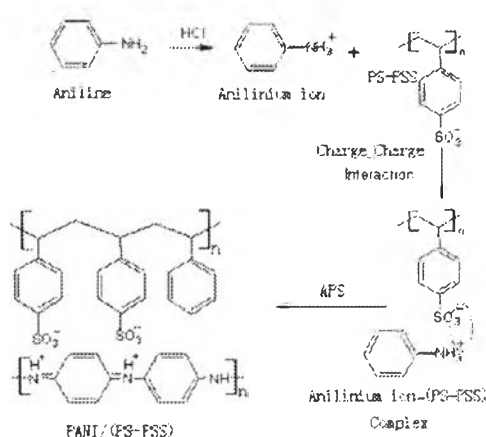
Figure 2.10 Mechanism of the synthesis of core-shell (PS-PSS)/PANI particles (Sun *et al*, 2011).

Li *et al.* (2012) were investigated effect of acidity on particle size. They synthesized polyaniline-poly(sodium 4- styrene sulfonate) (PSS) by oxidative polymerization. Aniline monomer in acid solution and PSS in APS in acid were prepared, mixed and kept it 24 hours to polymerization. They found that PANI-PSS/hydrochloric and PANI-PSS/camphorsulfonic acid had less stability in buffer solution (1, 7 and 11) than PANI-PSS/acitic acid when they were kept for a long time. PANI-PSS/CH$_3$COOH had less π-π^* conjugated length than others shown in UV-vis plot which had blue shift and polaron structure more localized. Their experiment could summarize that synthesis PANI with strong and weak acid led to large and precipitate, and small and stable colloid, respectively. Figure 2.11 showed that at low pH, PSS had electric-neutral form in strong acid so it loose negatively charge to interact with aniline protonated and became larger size than high pH. At high pH PSS had more salt form, could interact and stick aniline protonated on its chain, and became smaller size.

Low pH
polymerization

High pH
polymerization

Protonated aniline	styrenesulfonic anion on PSS
PSS main chain	Protonated PANI aggregate	PANI:PSS particle

Figure 2.11 Effect of pH and number of negatively charge group in PSS on the particle size of PANI-PSS composite.

2.3.1.6 In-situ Polymerization

Rubinger et al. (2009) synthesized polyaniline blend PSS by varing degree of sulfonation of polystyrene sulfonate that they synthesized also. They found that the conductivity of polymer increase with sulfonation degree because the more homogeneous polymer was, the more charge carrier flowing is. Therefore, the conductivity could control by degree of sulfonation.

2.3.1.7 Polymerization based on Temperature

Conducting films from poly(sodiumstyrene sulfonate) and polyaniline with layer-by-layer technique were investigated by Tang et al. (2009). They synthesized polyaniline fiber at high temperature by mixed aniline in hydrochloric acid at 80°C then added potassium peroxydisulfate (KPS) quickly. After all dissolved kept solution at 0-3°C for 10 hours. They found that if PANI was prepared at high temperature only, it could not grow because higher solubility. And if prepared PANI at low temperature only, it would have small quantity and crystal could not grow. All of these reasons, they prepared PANI by combination polymerization. Moreover, they found that the adsorptions were saturated after 5 minutes for PSS and 15 minutes for PANI of the deposition. The films had orientation PANI on the substrate as compared with conventional PANI that led to get higher conductivity. The number of layer could increase with conductivity and increase rapidly when number of layer was more than 4 due to connection of conducting channel. The roughness films were decrease when increase number of layer because of compensation effect.

2.3.1.8 Interfacial Polymerization

Electrically conducting polyaniline nanofiber composite was prepared by interfacial polymerization and investigated by Hopkins et al. (2004). Interfacial polymerization consisted of two layer solutions which were organic layer and aqueous layer. Organic layer had aniline monomer dissolved in CCl_4 and aqueous layer had APS and PSS. It was believed that aniline monomer was protonated with polyacid or PSS at interface following figure2.12 and then formed head to tail coupling for low energy helical structure when polymerized into aqueous layer, solution became green solution. PANI succeeded in 40-50 nanometers. They

found that PSS could act as dopant, stabilization and charge carrier. Moreover, electrical conductivity increased with % weight PSS in PANI nanofiber.
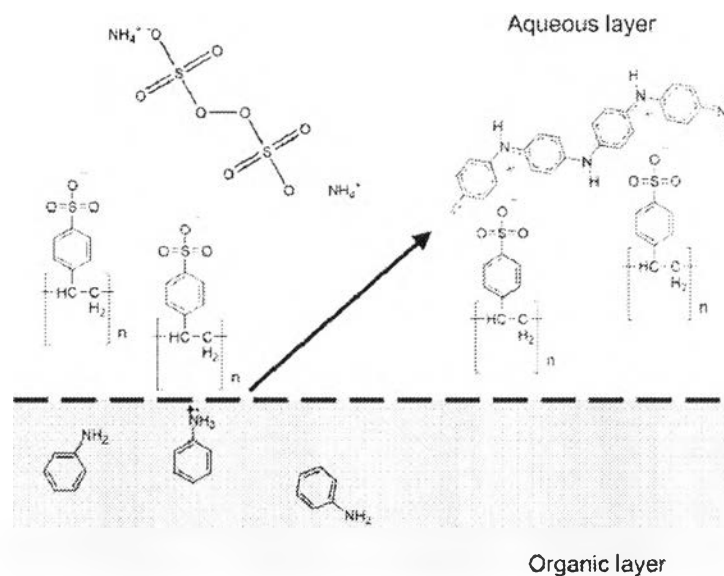
Figure 2.12 Interfacial polymerization the top layer was an aqueous solution while the bottom layer was organic layer.

Ratio of aniline monomer to PSS had effect on shape of polyaniline investigated by Kuo and Wen (2008). They synthesized polyaniline nanoparticles in aqueous PSS by interfacial polymerization route. Organic phase had aniline in chloroform and aqueous phase had PSS and APS. They found that polyaniline could disperse in aqueous phase because of strong electrostatic between anilinium and sulfanate group. Ratio aniline to PSS had effect on shape of PANI, spherical particle PANI was observed at ratio 1/1, nanoparticle or short-rod PANI and network PANI were observed when ratio less than 1 and more than 1, respectively. Network PANI was core of PANI-PSS and shell of excess PSS. Nanoparticle was spherical PANI which could not formed core-shell because fewer amount and lower viscosity of PSS so it could not lead to micelles.

Process1: Unsaturated doping

Process2: Saturated doping
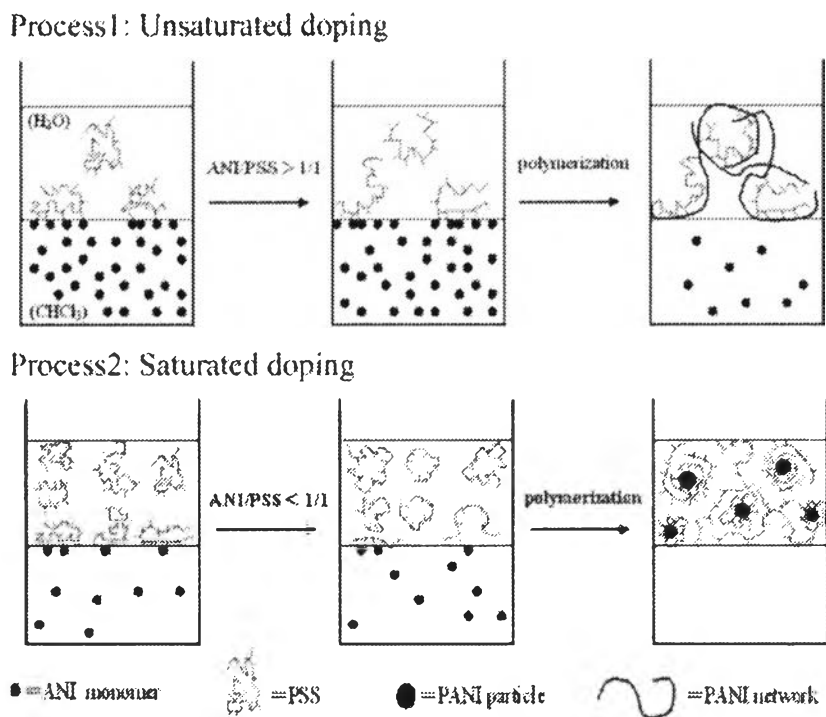
Figure 2.13 Polyaniline particle and network.

The effect of monomer concentration on interfacial synthesis of platinum loaded polyaniline nanocomplex using poly(styrene sulfonic acid) was investigated by Cho et al. (2011) who compared polymerization of polyaniline by interfacial and non-interfacial polymerization also. The way to enhance conductivity of conducting polymer or polyaniline was incorporate metal. In their work platinum (Pt) precursor well-known very expensive was used as oxidizing agent. Interfacial polymerization including aniline monomer in chloroform at lower phase and Pt-PSS in water at upper phase got green solution while purple solution got from non-interfacial polymerization including aniline monomer Pt-PSS without chloroform so it was not phase separate. They found that non-interfacial polyaniline synthesis had low conductivity because it had full oxidation state but high conductivity by using interfacial polyaniline synthesis due to it had half oxidation state. They varied concentration of aniline monomer; ANI:Pt = 4:1, 10:1 and 40:1, to observe current density and found that mole ratio ANI:Pt = 10:1 had highest value because it had small particle size nanocomposite contributed to improve electrochemical properties.
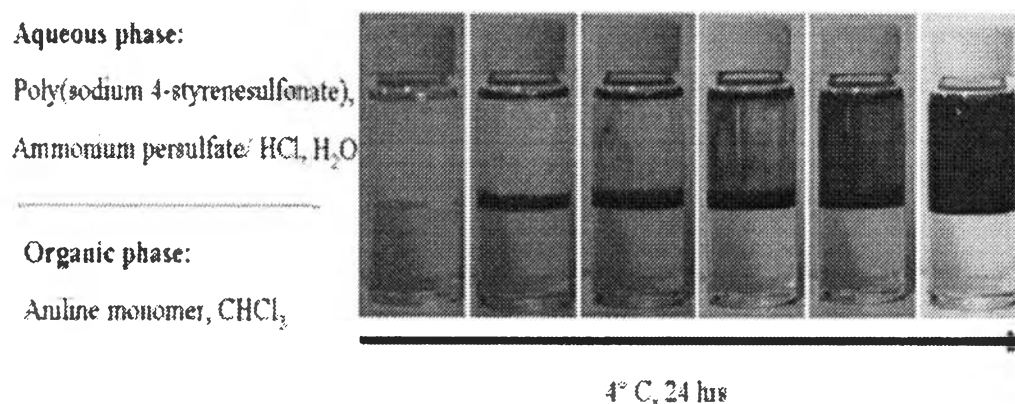
Morphology of them showed that roughness increased with monomer concentration and particularly, at over 20 concentration of monomer became thicker and straight fibril occurred because of secondary growth of polyaniline.
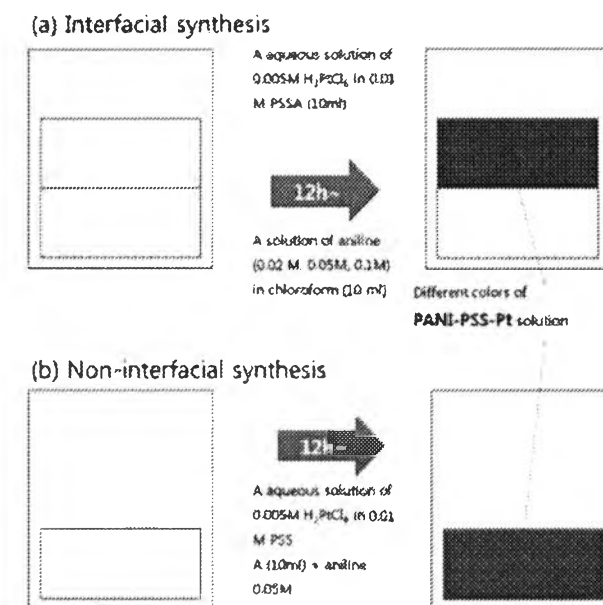
Figure 2.14 Preparation process of (a) PANI-PSS-Pt in interfacial and (b) in non-interfacial synthesis.

Electrostatic was very useful for polymerization that Detsri and Dubas (2012) used to provided water-soluble polyaniline by interfacial polymerization because normally polyaniline could not soluble in water and became the limitation of layer-by-layer technique that they use to make thin films. They synthesized water-soluble polyaniline succeeded between two phase; aqueous and organic phase. Aqueous phase, poly(4-styrenesulfonate) sodium salt(PSS) used as anionic dopant and template ,and diammonium persulfate (APS) as oxidizing agent, this phase was prepared in hydrochloric acid. Organic phase, aniline in chloroform was prepared. Solution was kept it in 4°C for 24 hours. Water-soluble polyaniline blend PSS began at the interface first and then polymerized into aqueous. They found

that they got highest yield at 50 mM PSS concentration but to make films with layer-by-layer technique at 10 mM PSS concentration had highest absorbance and conductivity because at 50 mM PSS concentration had excess in solution and become competition to absorb on substrate. They found many parameters affected to films growth such as film growth increased with concentration of NaCl, number of layer, conductivity increased with number of layer and thickness was highest at 10 mM PSS concentration because of competition of excess polymer.

Aqueous phase:

Poly(sodium 4-styrenesulfonate),

Ammonium persulfate/ HCl, H₂O

Organic phase:

Aniline monomer, CHCl₃

4° C, 24 hrs

**Figure 2.15** The interfacial synthesis of polyaniline with PS as template.

2.4 Nanocomposites based on Polyaniline

Gas sensing behavior of multi walled carbon nanotube polyaniline composite films was investigated by Srivastava *et al.* (2009). They prepared polyaniline by in situ chemical oxidative polymerization and used polyaniline to prepare PANI/CNT composite. They found that composite could enhance conductivity compared to pure polyaniline due to multi walled nanotube had higher surface area, gas absorption, sensitivity and stability and polyaniline was conducting polymer when they become composite had more gas absorption, sensitivity and charge transfer. Resistivity was increase with amount of hydrogen gas absorbed.

Gheno *et al.* (2011) investigated polyaniline had been grown among the graphene sheet. They synthesized polyaniline/graphite nanocomposites by intercalate aniline monomer through pores and galleries of graphite sheet exfoliate. Graphite

nanosheets (GNS) were prepared by using intercalation, expansion and exfoliation. Then, pure aniline monomer was mixed with GNS after that, ethanol, HCl and APS were added. They found that the volume of intercalated graphite increased three times compared with natural graphite flake. The uniform distribution of nanosheets retained after intercalation and expansion with strong acid and high temperature following figure 2.16. They showed the results that thermal stability was higher when nanocomposites had more graphite content and electrical conductivity increased too much when %wt of PANI increase. Particularly, conductivity increased ten times when compared with pure neat polyaniline.
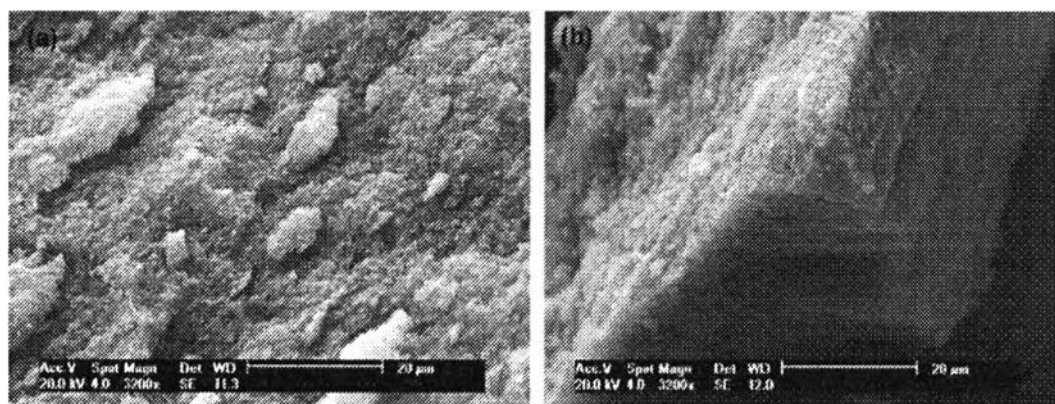

Figure 2.16 SEM image (a) neat polyaniline (b) PANI/GNS nanocomposite.

Hussian et al. (2012) polymerized polyaniline/polypyrrole/polythiophene and functionalized multiwalled carbon nanotube-based nanocomposites by using layer-by-layer in-situ technique. Functionalization of multiwalled carbon nanotubes (F-MWCNTs) was prepared by annealed and acid treatment raw MWCNTs. Polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh), respectively were synthesized on surface of F-MWCNTs following figure 2.17. They found that F-MWCNTs reinforcing matrix polymer had high specific surface areas which could provide large number of sorption sites to the monomer. Polymer wrapped around MWCNTs and nanocomposites agglomerated when material had low F-MWCNTs concentration while high F-MWCNTs had no any agglomerate polymer according to figure 2.18.

Nanocomposites had higher thermal stability than F-MWCNTs because the major weight loss was polymer degradation that covered on F-MWCNTs. Electrical conductivity of nanocomposites was higher (413 S cm^{-1}) than three of each polymer (PANI, PPY and PTh were 30, 10-40 and 1.23×10^{-4} S cm^{-1}, respectively) due to fine dispersion of F-MWCNTs in the polymer matrix.
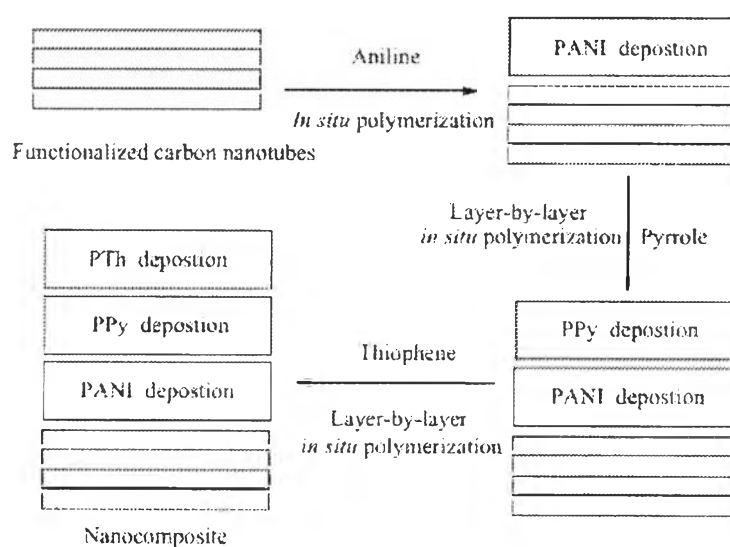

Figure 2.17 Fabrication of PANI/PPy/PTh/F-MWCNTs through layer-by-layer in situ polymerization.
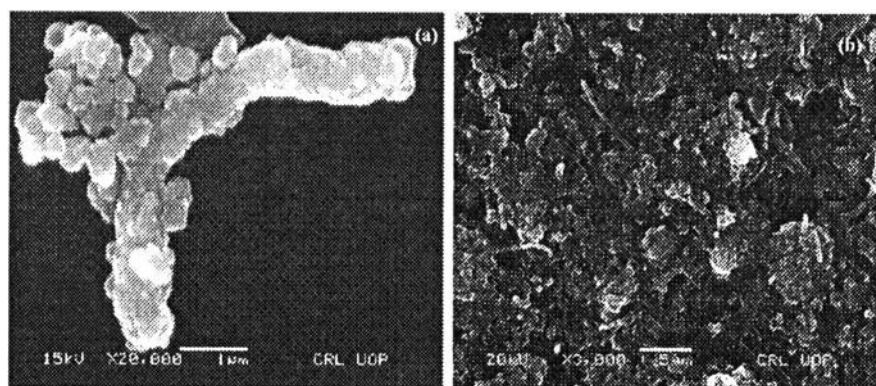

Figure 2.18 FESEM images of (a) PANI/PPy/PTh/F-MWCNTs (low CNTs concentration) and (b) PANI/PPy/PTh/F-MWCNTs (high CNTs concentration).

Benjamin *et al.* (2008) created surface patterning on silicon which had both hydrophobic and hydrophilic regions for polyaniline and carbon nanotube deposition. There were two types of silicon substrate. One had $-CH_3$ group at the edge and $-NH_2$ group in the middle and another had $-OH$ group in the middle. They found that polyaniline prefered the $-CH_3$ group to polymerize due to $-CH_3$ group was hydrophobic that liked aniline monomer, like dissolved like principle, following in figure 2.19. Polyaniline covering on the $-CH_3$ region occurred green color which showed the wavelength from UV-Vis spectra at 796 nm, indicating a protonation of imine site. The wavelength was shifted with changing color from green to blue at 602 nm. Conductivity of polyaniline on silicon substrate was 12.7 ± 3.4 σ/S cm^{-1}. Single-walled carbon nanotubes were treated with acid to create functional group for deposition on the functional group of $-NH_2$ and $-OH$ and had either ester or amide linkage. Then polyaniline was polymerized on it and the result showed that polyaniline cover all surface due to it could polymerize on $-CH_3$ group and surface of single-walled carbon nanotubes which was naturally hydrophobic and remained acid from nanotube treatment so polyaniline could polymerize on it, following figure 2.20. The conductivity of composite was not different when compared with polyaniline.
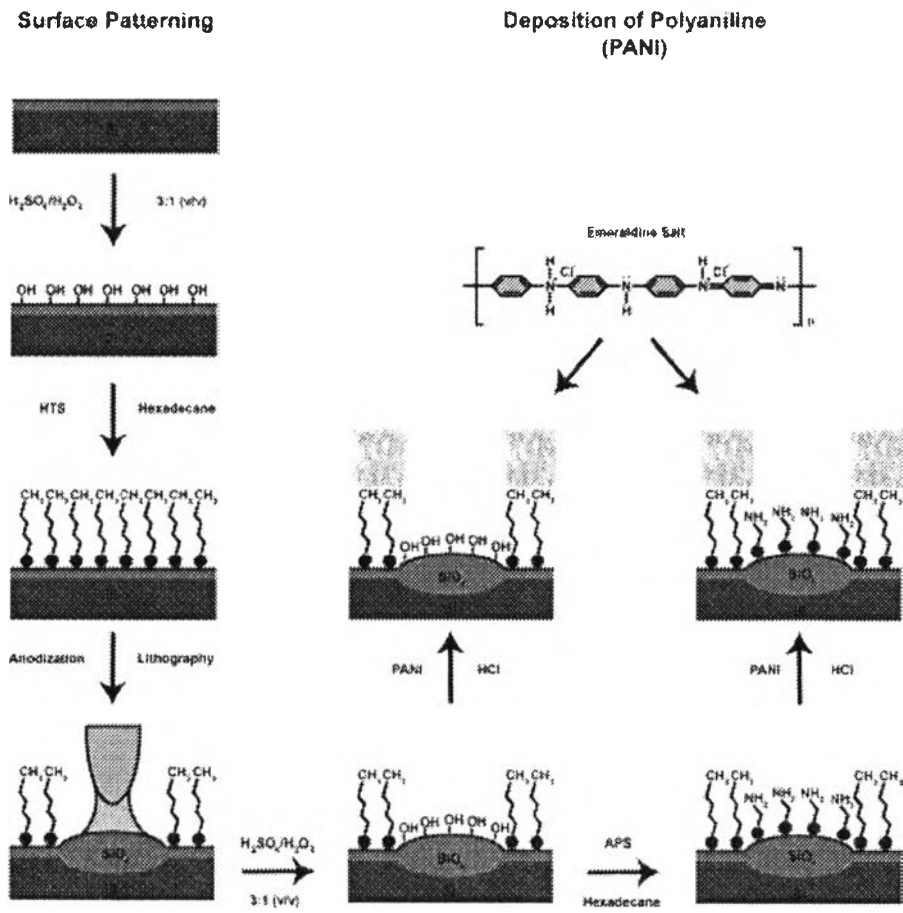
Figure 2.19 Creation of pattern hydrophobic/hydrophilic silicon to allow the selective deposition of polyaniline.
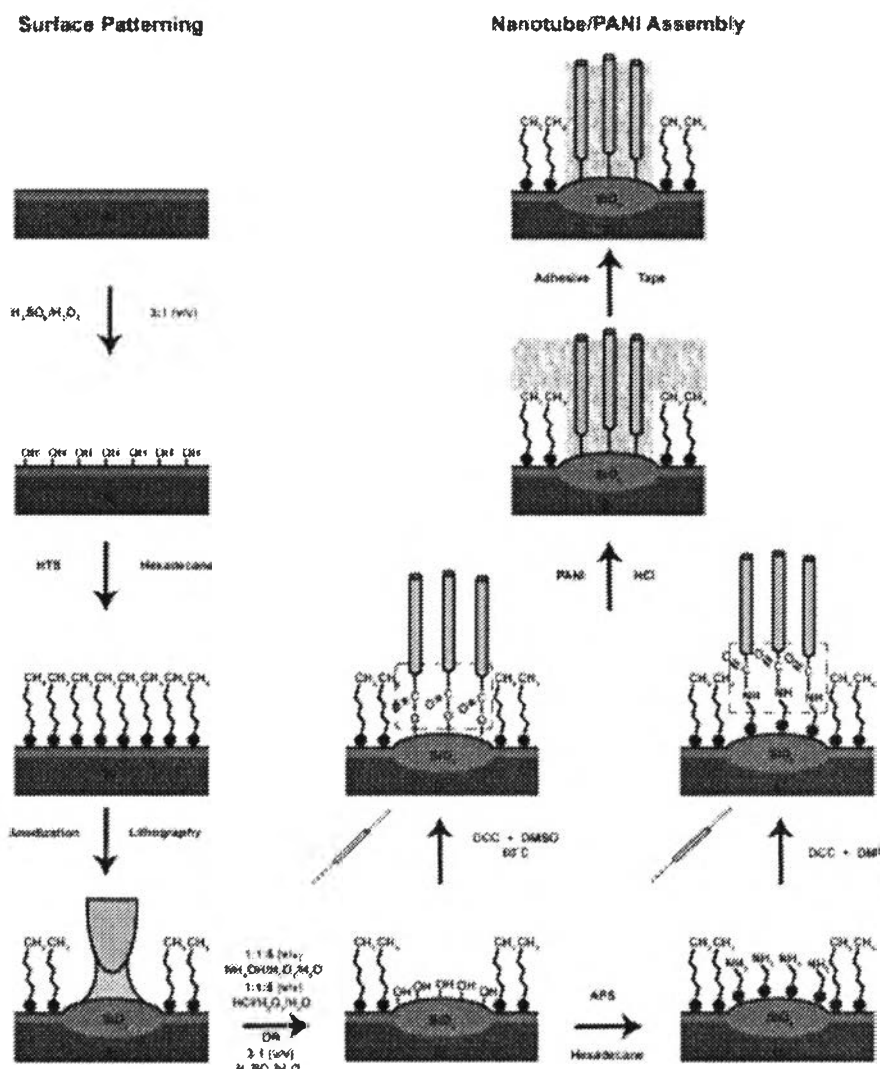
Figure 2.20 Patterned assembly of single-walled carbon nanotubes on silicon allows the creation of patterned carbon nanotube-polyaniline composites.