# CHAPTER II

# THEORETICAL BACKGROUND AND LITERATURE REVIEW

## 2.1 Conducting Polymer

Generally, polymers are a non electrical conducting material which are normally used as insulators. In 1970s, conductive polyacetylene was invented (Yamabe *et al.*, 1979). In 2000, the Nobel Prize was awarded to Alan J. Heeger, Alan G MacDiarmid, Hideki Shirakawa for the discovery and study of conducting polymers. The conducting polymers have been intensively studied since 1970s due to their interesting application such as sensors (Mekki *et al.*, 2013), conductive ink (Rajzer *et al.*, 2015), supercapacitors (Wang et al., 2009) and etc.

The advantage of conducting polymer are the various conducting level due to the doping level and maintain good mechanical properties, thermal properties and process ability.

### 2.1.1 Polyaniline

Polyaniline (PANI) is a conducting polymer which has an aniline as a monomer. Aniline monomers are polymerized by a oxidation polymerization.

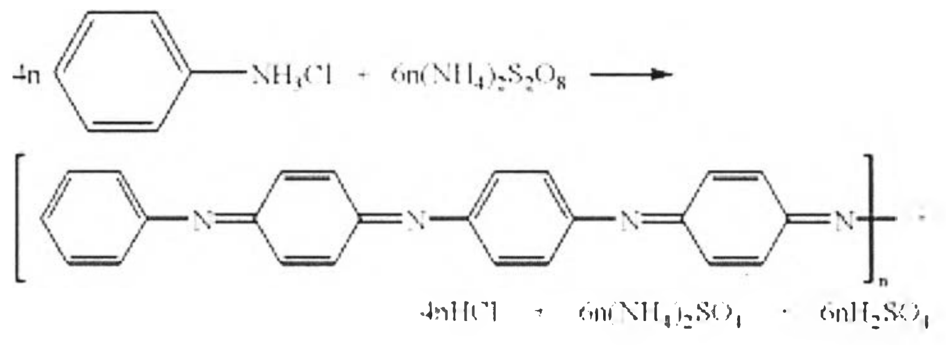

**Figure 2.1** Polyaniline polymerization.

The advantages of PANI are its environmental stability, controllable optical properties, conductivity which can be used in sensors, semiconductors, batteries, solar cells and etc. PANI has many forms with different properties. The conductive form of PANI is protonated emeraldine which is a semiconductor.

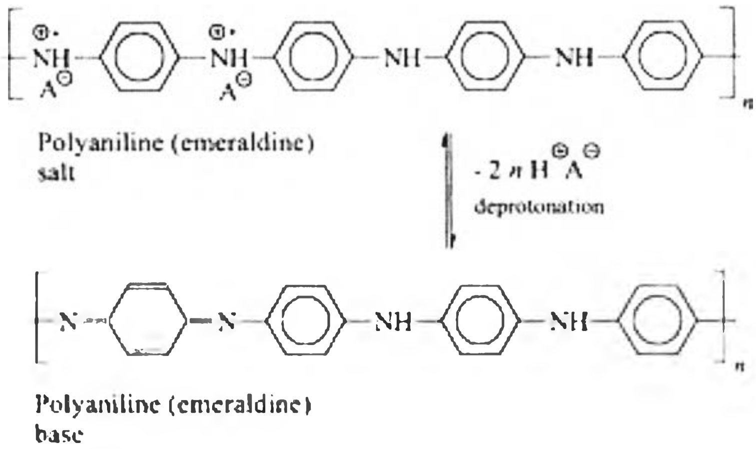

**Figure 2.2** Polyaniline (emeraldine) salt is deprotonated in thermal alkaline medium to polyaniline (emeraldine) base. A– is an arbitrary anion, e.g. chloride.

Yang *et al.* (1997) reported the properties of Polyaniline-Polyelectrolyte complexes. PANI-PAA and PANI-PSS complex were synthesized by mixing ANI monomers polyacid together and stirred follow by APS and HCl while stirring then let the solution for hours and dialyzed in an acid medium to remove unreacted monomers. The results showed that the protonation levels of PANI-PAA and PANI-PSS complexes were 22% and 84%. The oxidation state of PANI-PSS was higher than emeraldine salts. IR spectrum show peaks at 1570, 1490, 1305, 1120 and 800 $cm^{-1}$ which is emeraldine salt. The complexes formed with APS have no peak at 1240 cm-1 which is C-N stretching in BBB (B=benzenoid unit). Peaks at 1380 $cm^{-1}$ (C-N stretching in QBtQ, Q=quinoid unit) and 1135 $cm^{-1}$ (N=Q=N) are more significant. IR result indicates that PANI-PSS with APS has more oxidized and less reduced units. From UV-vis spectrum, PANI-PSS at pH 8 shows peaks at 800-900 nm and a shoulder at 420 nm which is emeraldine salt. At pH 11, there are peaks at 550-630 which is base form. PANI-PSS synthesized with APS and $H_2O_2$ shift to 553 nm and 573 nm indicating the higher oxidation state than emeraldine. Figure 2.3 shows an example of UV spectrum of PANI-PSS at varied pH.

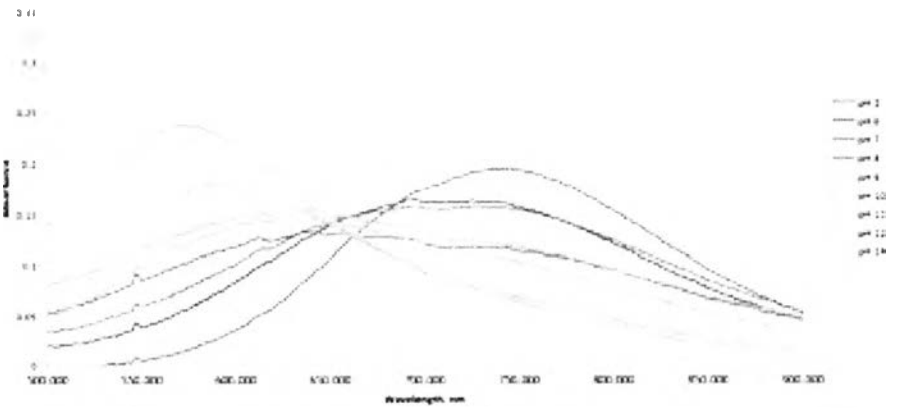

**Figure 2.3** UV spectrum of PANI-PSS at varied pH.

Jayanty *et al.* (2003) reported polyelectrolyte templated polyaniline on film morphology and conductivity. A stable colloidal solution of poly(4-styrenesulfonate) templates polyaniline was performed by oxidation polymerization using APS and HCl. The molecular weight of emeraldine salt PANI can't be calculated because of coexistence of polyionic chains in PANI-PSS. The higher molecular weight PSS leads to higher conductivity and promote extended and aligned PANI chains. The red shift of the polaronic band with the molecular weight of the template suggests that polyelectrolyte acts as a template, controlling the polymerize process.

Dubas *et al.* (2012) reported on interfacial polymerization of PANI. An interfacial polymerization of PANI was performed by adding PSS as a template and APS with HCl in upper aqueous phase and aniline monomer in $CHCl_3$ lower phase then the reaction was kept in 4 °C for 24 h.

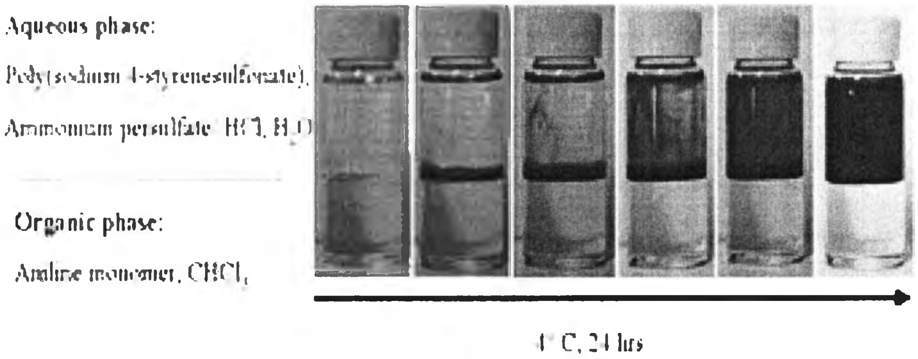

**Figure 2.4** Diagram depicting the interfacial synthesis of polyaniline with PSS as template.

The effect of ratio between aniline monomer and PSS in synthesis step was studied. PSS was used in excess to maximize the template effect of the PSS on PANI and improve its solubility which lead to unreacted PSS excess in solution which can be a problem in LbL deposition. PSS at 3 mM is a minimum condition to synthesize PANI and PSS at lower than 3 mM, PANI precipitate at the interface. At PSS concentration more than 50 mM, the polymerization rate decrease because go the higher viscosity due to the PSS concentration. The template effect can be explained by the strong electrostatic interaction between $SO_3^-$ of PSS and $NH_3^+$ of PANI and π-π interaction between the benzene rings on PSS and aniline.

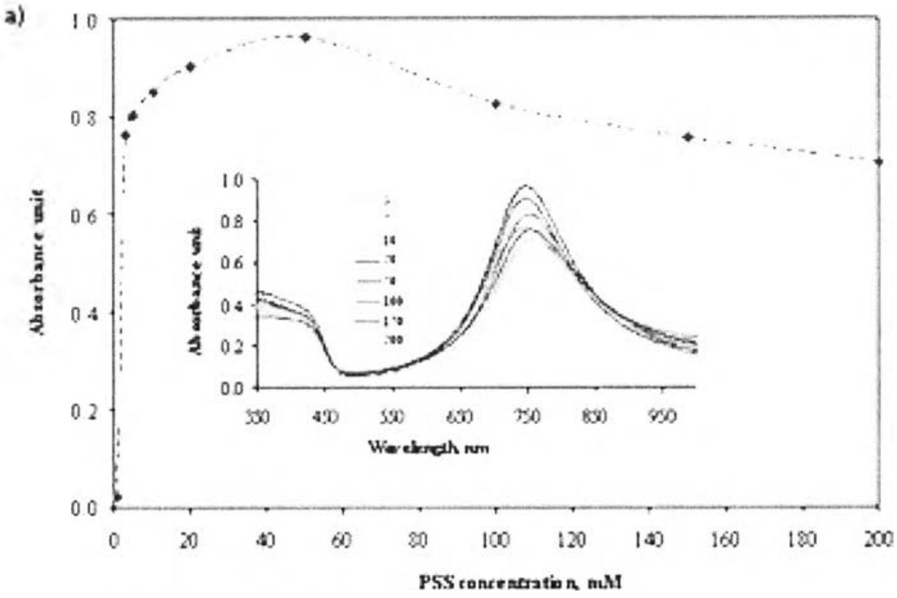

**Figure 2.5** Plot of the change in absorbance of the aqueous phase after interfacial polymerization as a function of PSS concentration.

The interfacial polymerization of PANI has benefits over bulk polymerization which are the rate of reaction is slower due to the separation between monomers and initiators and the ability to remove monomers in interfacial polymerization is better than bulk polymerization so the interfacial polymerization is more controllable.

## 2.2 Polyelectrolytes

Polyelectrolytes are polymers that have electrolyte group in repeating units and those electrolyte group can be dissociate in aqueous or water, making polymer chain charged. Polyelectrolytes can be divided in 2 types which are polycations and polyanions and can be classified as weak and strong polyelectrolyte which has $pK_a$ and $pK_b$ similarly to acid and base. Polyelectrolyte can be use in many applications, often used as thickeners, emulsifiers, conditioners and clarifying agents and also use in soaps, shampoos, cosmetics, biochemical and medical applications.

### 2.2.1 Polystyrene Sulfonate (PSS)

Polystyrene sulfonate (PSS) is a water soluble polyelectrolyte which is polyanion that has $pK_a = 2$. Polystyrene sulfonate derive from sulfonation of polystyrene. Polystyrene sulfonate can be use as a template for synthesizing water soluble polyaniline. PSS can be use in water softening and medical applications via their ion exchange properties.

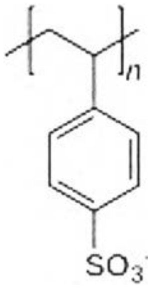

**Figure 2.6** Polystyrene sulfonate (PSS)

### 2.2.2 Poly(sodium 4-Styrenesulfonaic Acid-Co-Maleic Acid) (CoPSS)

Poly(sodium 4-styrenesulfonaic acid-co-maleic acid) (CoPSS) is a water soluble anionic polyelectrolyte that contains both sulfonate and carboxylate groups which are strong and weak charging units.

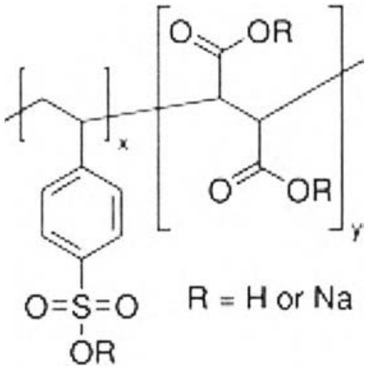

**Figure 2.7** Poly(sodium 4-styrenesulfonaic acid-co-maleic acid) (CoPSS)

### 2.2.3 Polydiallyldimethylammonium Chloride (PDADMAC)

Polydiallyldimethylammonium chloride (PDADMAC) is a water soluble cationic polyelectrolyte that synthesized by radical polymerization of DADMAC by organic peroxide. PDADMAC can be use as a coagulant in water purification.

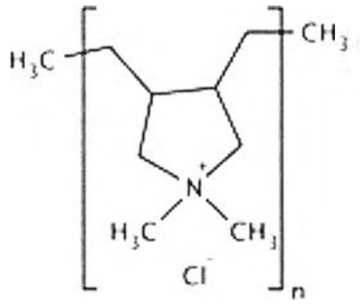

**Figure 2.8** Polydiallyldimethylammonium Chloride (PDADMAC)

## 2.3 Layer-by-Layer Assembly

Decher *el al.* (1991) reported on consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces.The layer-by-layer assembly was performed by using boladianion and boladication. In order to avoid loop formation they use central biphenyl unit as a rigid core in amphiphile and by using this two dipolar amphiphiles, it is possible for doing multilayer assembly. For the adsorption of the first layer, acidic solution was used to protonate the amino groups on the surface then continually dip in boladianion and boladication alternately and respectively.

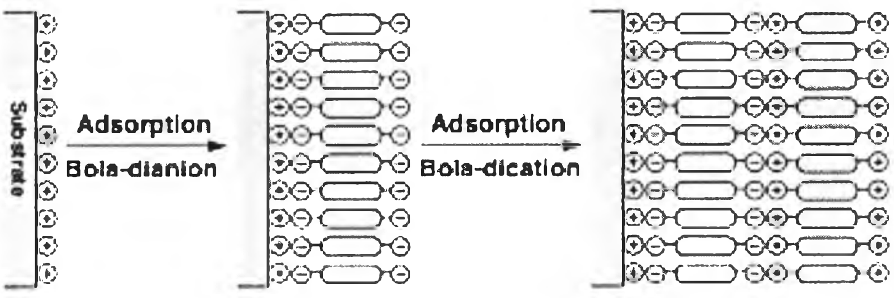

**Figure 2.9** Schematic representation of adsorption of bipolar molecules on a charged surface.

Dubas el al. (1998) reported on the factors controlling the growth of polyelectrolyte multilayers. The adsorption of polyelectrolyte onto oppositely charged substrate is an ion exchange process where charged segment replace small ions from salt compensating the surface change. At low salt concentration, polyelectrolytes are efficient to find and adsorb on oppositely charged surfaces. At some point of high salt concentration, salt ions are sufficient to displace all the polymer from the surface. The thickness of the film is linearly proportional to the

NaCl concentration between $10^{-2}$ to 2 M. The adjunction of salt will screen the electrostatic interactions within the polyelectrolytes which neutralized the ionic groups.

Tang *el al.* (2009) reported on the layer-by-layer self assembly of conducting multilayer films from poly(sodium styrenesulfonate) and polyaniline. PANI fiber was polymerized using ANI monomer at high temperature and growth in low temperature by aqueous oxidation polymerization. The layer by layer between PSS/PANI was prepared with PANI fiber and PANI powder form. The dipping time of PSS was 5 min and PANI was 15 min. The deposition of PSS and PANI is due to an ion exchange because of the adsorbing of PSS and PANI result in the decreasing entropy. Equilibrium deposition can be obtained when PSS or PANI chains are repelled from the surface. Between PSS and PANI, there are hydrogen bonding interactions between the N-H group in PANI conjugated chain and the oxygen atom in PSS. AFM was used to study the morphology of the film and the result showed that the gain size of PANI increased at higher thickness because of the aggregation of PANI. A very smooth surface can be obtained by more deposition cycle. The conductivity of film is increase with number of layers and the conductivity of oriented PANI fibers is much higher than conventional PANI powders.

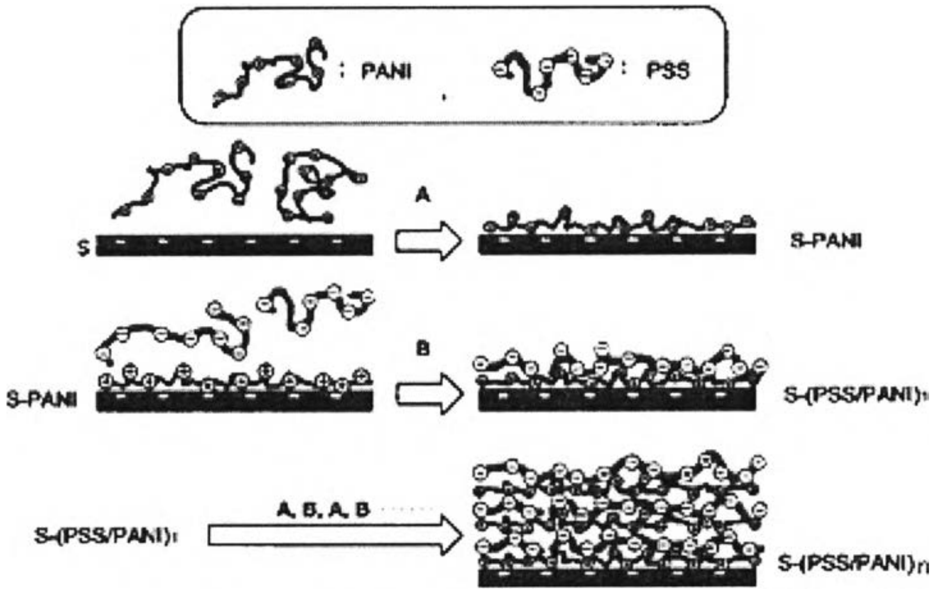

**Figure 2.10** The self-assembly process of (PSS/PANI)n multilayer films. Step A was the deposition of PANI layer; step B was the deposition of PSS; by repeating A and B, (PSS/PANI)n multilayer films were obtained.

## 2.4 Silver Nanocomposite

Mekki *et al.* (2013) reported $H_2S$ sensing using in situ photo-polymerized polyaniline-silver nanocomposite film on flexible substrates. Polyaniline-silver nanocomposite on (3-aminopropyl)trimethoxysilane (APTMS) modified biaxially oriented polyethylene terephthalate (BOPET) was prepared in a glass bottle containing BOPET and aniline monomer by protonating aniline monomer with $HNO_3$. Then added $AgNO_3$ and placed under UV lamp set at wavelength 365 nm, UV source to sample distance 13 cm, intensity 5 mW/cm$^2$ for 6 h to polymerize polyaniline and reduced $Ag^+$ to $Ag^0$ . Then washed with DI water and exposed the film to HCl vapor for 2 min. finally the sample was dried for 4 h at 70 °C in an oven.

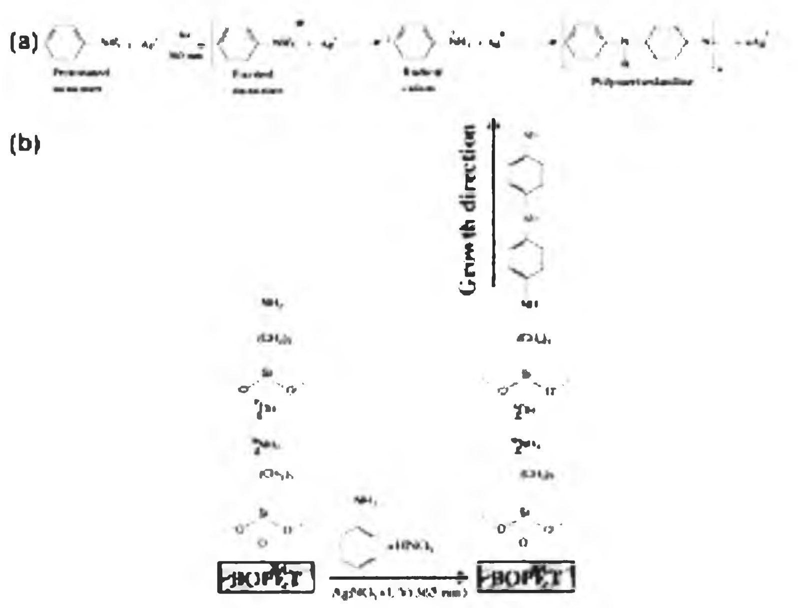

**Figure 2.11** Scheme showing the surface modification of BOPET substrate by APTMS.

By using this synthesis approach cause the improvement of adhesion of deposited polyaniline-silver films and provide brush like morphology. Chemiresistive gas sensing characteristic were observed for different $AgNO_3$ concentration that were used in the synthesis step. The result showed that at higher Ag content the conductivity increased but at concentration of $AgNO_3$ that higher than 3 M, the conductivity dropped because of Ag clusters that could form schottky barriers and therefore lower the conductivity. Polyaniline-silver nanocomposite film showed the response for only $H_2S$ at 10 ppm exposing but didn't response to $NH_3$, $Cl_2$, NO, $NO_2$, CO, $CH_4$ and $C_2H_5OH$.

Mironenko *et al.* (2014) reported the fabrication and optical properties of chitosan/Ag nanoparticles thin film composites. Chitosan/Ag thin film was prepared by immersed chitin film into $4x10^{-4}$-$5x10^{-3}$ M of $AgNO_3$ solution then vary dipping time from 5 to 120 min to find the optimum diffusion time of $Ag^+$ in chitosan film. washed the film with running DI water to remove the $Ag^+$ at the film surface then immersed the film into 0.001-0.1% NaBH4 for 30 min to reduce $Ag^+$ to $Ag^0$. the results showed that absorption process reach quasi equilibrium at 10 min of dipping time and the optimum concentration of $NaBH_4$ is 0.01% solution but at concentration that is higher than 0.05% cause the film to rupture due to intensive hydrogen release. UV-vis spectra of chitosan/Ag thin film showed absorption band at 412-413 nm due to silver in the film. The absorption band of chitosan/Ag thin film is red shifted up to 12 nm which cause by the growth go reflective index of the media around metal nanoparticles due to the polymer absorption and cause by particles agglomeration. The position of absorption band depends on Ag/chitosan, the higher silver content, the lower the wavelength of maximum plasmon adsorption due to the difference in size of silver particle with different chitosan concentration or the different thickness of polymer shell around metal particles.

Anandhakumar *et al.* (2013) reported polyelectrolyte/silver nanocomposite multilayer film as multifunctional thin film platforms for remote activated protein and drug delivery. They prepared nanoparticles synthesis in the PEMs by dipping preassembled poly(allylamine hydrochloride) (PAH) / dextran sulfate (DS) multilayers (6 bilayers) into 25 M and 50 M of $AgNO_3$ at pH 6 for 1 h. $Ag^+$ diffused and exchanged with acid protons of $SO_4^-$ group in DS. Then washed to remove $Ag^+$ at the surface and reduced $Ag^+$ to $Ag^0$ and regenerated $SO_4^-$ which can be used for further multilayer assembly by dipping in 2.5% PEG at 50 °C for 1 h. Normally the reduction often use hazardous chemical such as $NaBH_4$, dimethylformamide or hydrazine but PEG is a biologically safe material which can be used as a reducing agent and stabilize the silver nanoparticles.

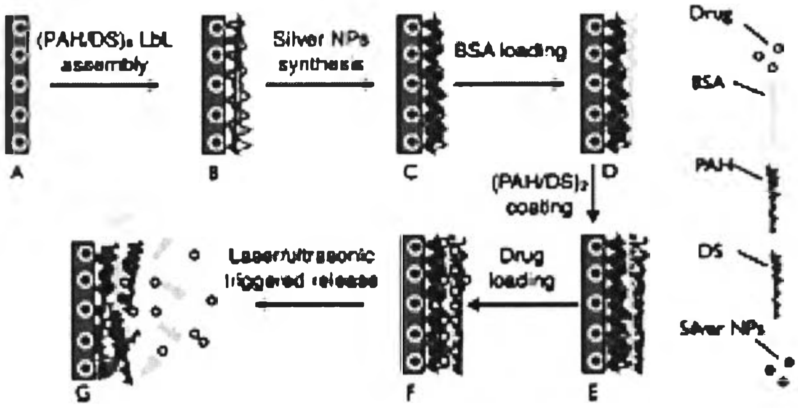

**Figure 2.12** Schematic of the methodology for the fabrication of PEM films for remote activated drug and protein delivery. A, glass substrate; A–B, LbL deposition; B–C, silver NP synthesis; C–D, BSA loading; D–E, additional (PAH/DS) layer deposition; E–F, CH loading; F–G, remotely activated release.

The result showed that $AgNO_3$ concentration effected the size, distribution and concentration of silver nanoparticles in the film. The silver nanoparticles in the film showed a yellow color as a result of the surface plasmon resonance of the conduction electrons. At higher concentration of $AgNO_3$ showed a metallic and shiny surface due to the aggregation of silver particles. When silver nanoparticles aggregate the localized surface plasmon resonance effect decrease as the electron path length is altered.

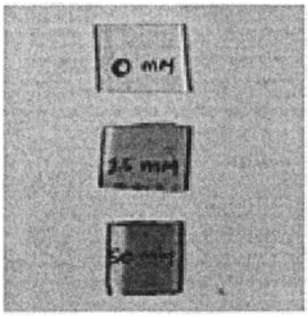

**Figure 2.13** Visual transparency of films incorporating NPs as a function of $AgNO_3$ concentration. The pure film appears colorless, but becomes metallic brown when the concentration is increased to 50 mM.

Liu *et al.* (2005) reported silver nanocomposite layer by layer films based on assembled polyelectrolyte/dendrimer. The silver nanoparticles were synthesized in the the film by dipping PSS/dendrimer and PAA /dendrimer multilayers into 5 M of $AgNO_3$ for 24 h. Then washed with DI water to remove $Ag^+$ at the surface and dried in vacuum at room temperature. Then $Ag^+$ was reduced to $Ag^0$ in a hydrogen atmosphere (2 atm, 85 °C) for 24 h. The result showed the optical spectrum of small isolated silver particle in a dielectric matrix is dominated by a strong dipole absorption mode due to the collective oscillation of conduction electrons, the so-called surface plasmons. The silver nanoparticles absorbance increases with the increase of the number of layers. Silver nanoparticles in the PAA/dendrimer films was much higher than that in the PSS/dendrimer films because PAA is weak polyelectrolyte which can redistribute during the deposition cause the thiner in dimension and carboxylic acid group of PAA has an electrostatic interaction with $Ag^+$.

Dubas *el al.* (2006) reported the polyelectrolyte assisted silver nanoparticles synthesis and thin film formation. The silver nanoparticles were synthesized by using copolymer of polystyrene sulfonate and carboxylate as a capping agent then deposited the silver nanoparticles into multilayers thin film using the layer-by-layer assembly. The effect of polyelectrolyte concentration was studied and the results showed that increasing of polyelectrolyte concentration cause a broadening of the spectrum and red shift of the absorbance due to a broader distribution of silver particles size because diluted polyelectrolyte could cap silver more efficiently.

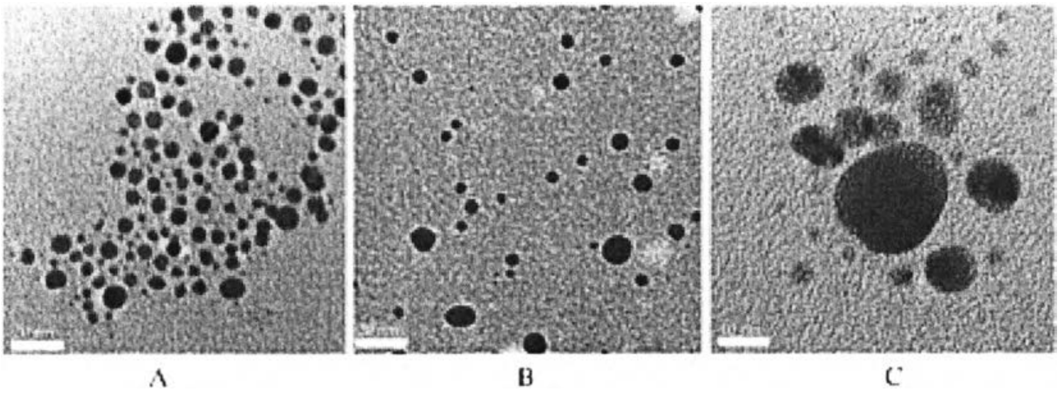

**Figure 2.14** TEM of the synthesized silver nanoparticles from various PSS-co-Maleic and silver nitrate molar ratio. (A) PSS-co-Maleic:silver nitrate = 0.5 mM:1 mM; (B) 1 mM:1 mM; (C) 2 mM:1 mM.

Guo *et al.* (2012) reported the fabrication and tribological properties of polyelectrolyte multilayers containing in situ gold and silver nanoparticles.

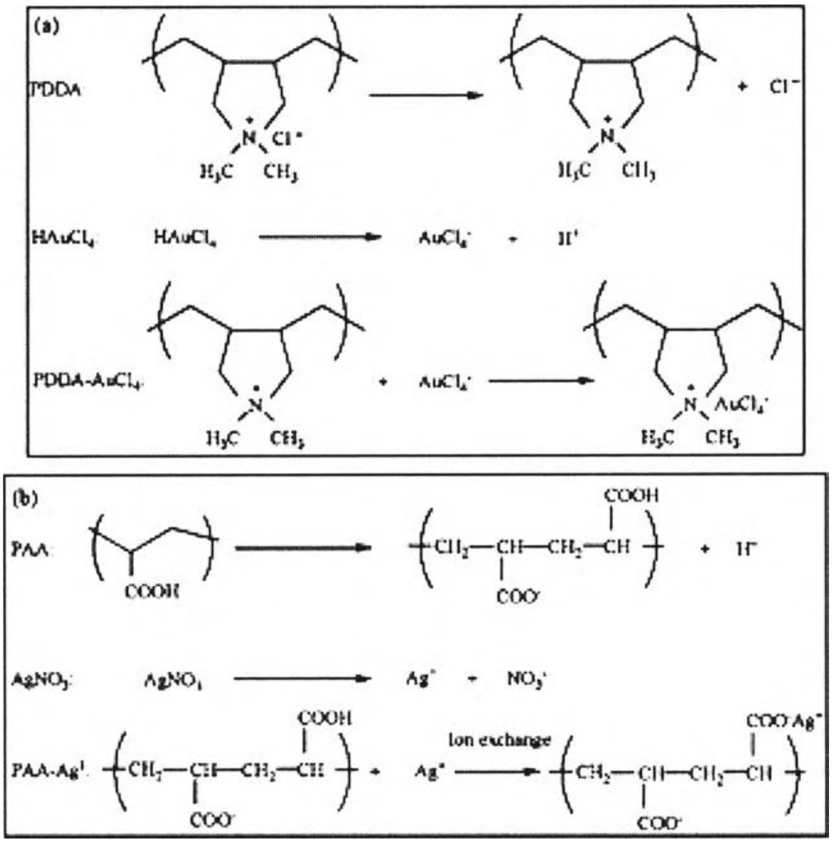

**Figure 2.15** Electrolytic formulas of reagents: structures of (a) PDDA–AuCl4$^-$ and (b) PAA–Ag$^+$ complexes.

Gold and silver nanoparticles in polyelectrolyte multilayers film can be prepared by immerse a substrate in poly(diallyldimethylammonium) chloride (PDDA)–AuCl$_4^-$ complexes solution and poly(acrylic acid) (PAA)–Ag$^+$ complexes solution for 30 min alternately then reduce Au$^{3+}$, Ag$^+$ with NaBH$_4$ solution for 10 min.

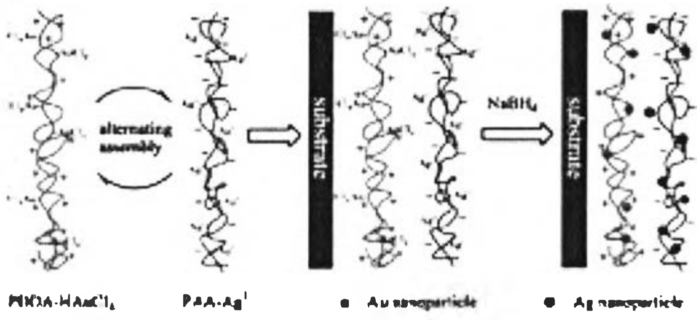

**Figure 2.16** Schematic of the layer-by-layer buildup and gold and silver nanoparticles formation process.

From the UV-vis spectrum, the ratio of Au/Ag absorbance value increased with the number of bilayers. Because in the washing step, some weak bond Ag+ ions were released because PDDA is a strong polyelectrolyte but PAA is a weak polyelectrolyte causing a strong bonding between $AuCl_4$ ions and PDDA and a weak bonding between $Ag^+$ ions and PAA. XPS was used to characterize Au and Ag in the film.