

## CHAPTER II

# BACKGROUND AND THEORY



### 2.1 Nanotechnology and nanosensors

#### *2.1.1 Introduction to nanotechnology*

Nanotechnology is currently one of the most actively studied research fields. The term nanotechnology and nanoscience need to be clarified since they are often misused. Nanotechnology is a term used to represent the design of nanomaterials for the development of a certain applications or products whereas nanoscience concerns the study and characterization of their physical properties [6]. Many definitions of "what is nanotechnology" proposed in the past few decades indicate that nanotechnology covers a wide range of research fields with researchers having very different areas of expertise. This variety is what makes nanotechnology so exciting as it encompasses many disciplines and requires truly interdisciplinary and multidisciplinary efforts. Although high expectations have been put into the development of new nanomaterials, very few products have appeared in our day to day life. Among all the nanomaterials under development, it is probably the single wall and multi-wall carbon nanotubes that have sparked the most excitement due to their exceptional electrical and mechanical properties [1-5].

Materials in the micrometer size scale mostly exhibit physical properties similar to that of bulk form. However, materials in the nanoscale may exhibit physical properties distinctively different. For instance the melting point of the same metal in the bulk or nanoscale can be as different as  $1000^{\circ}\text{C}$  due to the much higher fraction of surface atoms having an effect on the thermal stability. Other difference between bulk and nanomaterials can be found in gold since although bulk gold is known to be inert, yet, gold nanocrystals appear to be excellent low temperature catalyst and have been used for the oxidation of carbon monoxide (CO) to carbon dioxide ( $\text{CO}_2$ ) [7]. The automotive industry is indeed very interested and catalytic exhausts are being developed with gold nanoparticles in order to reduce CO emissions.

Although nanomaterials research is currently one of the most active research areas, the study of biological systems and the engineering of materials such as colloidal dispersion, metallic quantum dots and catalyst have been going on for centuries. More than a thousand years ago, across the world, Chinese and Italian used the brilliant red color of gold nanoparticles as pigment in porcelain and churches stained windows. Even earlier, Egyptian recognized the healing power of gold colloids solutions as well as the anti-microbial power of silver nanoparticles. Nanoparticles were even used in art pieces such as the Lycurgus cup at the British museum (Figure 2.1) which contains gold nanoparticles giving the color effect whether the piece is illuminated with front or back light. Since then, what has been changed in current time is only human ability to image, engineer and manipulate systems of the nanometer scale.



Figure 2.1: "The Lycurgus cup", art piece from the British museum containing gold nanoparticles

The fabrication of nanomaterials and nanostructures leads to materials which can be classified in various manners. One method is to group nanomaterials according to their growth media such as vapor phase, liquid phase, solid growth or hybrid growth. Another way to group nanomaterials is according to their shape such as nanoparticles

(Figure 2.2 A), nanorods (Figure 2.2 B), nanowires, thin films or nanostructures bulk materials. Among all the nanomaterials under development, nanoparticles are the most diverse nanomaterials. They include metallic (Au [13], Ag [11], Cu [16], Pt [20]), oxide (ZnO [8], TiO<sub>2</sub> [10], MgO [18], SiO<sub>2</sub> [17]), inorganic (ZnS [19], CdSe [15]), and organic nanoparticles (Chitosan or surfactant self assembled micelles) [9,14].

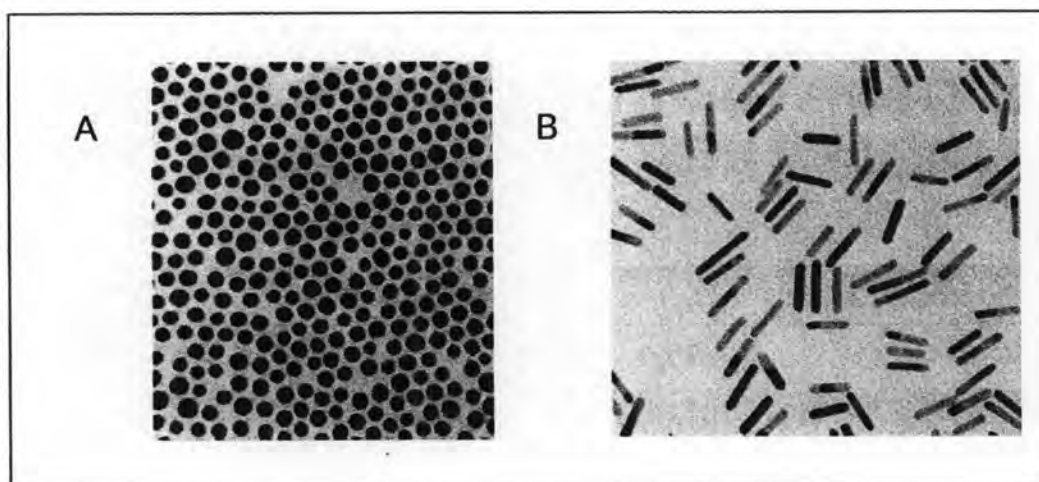


Figure 2.2: (A) Gold nanospheres and (B) gold nanorods

Nanomaterials such as nanoparticles, fullerene derivatives (buckyballs) and quantum dots have received enormous attention to create new types of analytical tools for biotechnology and life sciences [21]. Single wall and multi-walls carbon nanotubes have also received a great deal of interest for their potential applications in electronics and sensors [1-5]. Nanoparticles recently have also been developed for biomedical applications especially for targeted drug delivery systems. Although nanomaterials are currently being widely used in modern technology, there is a serious lack of information concerning the human health and environmental implications of nanomaterials. The major toxicological concern is the fact that some of the manufactured nanomaterials are redox active [22,23], and some particles transport across cell membranes and especially into mitochondria [23]. Recent work raised alerts against the danger of certain type of nanoparticles. In their work, Silver nanoparticles appear to be toxic by depleting the antioxidant defense mechanism, which leads to reactive oxidant species (ROS) accumulation [127]. All these findings suggest that more work is needed to

understand and control the toxic potential of nanoparticles based technology before nanomaterials are commercialized and could potentially harm the public.

### 2.1.2 Nanosensors

One of the areas in nanotechnology which has received a lot of interest concerns the design of nanosensors for detecting biomolecules, pollutants and other chemicals. Nano-biosensors are usually composed of a biological or biomimetic sensing element, a transducer and an amplifier for data collection and analysis [28,29]. While the most commonly used biosensor is probably the portable glucose sensor for insulin dependant patients, a wide range of biosensing devices has been developed. The bio-recognition elements can include antibodies [30], enzymes [31] or nucleic acid [32] which can be very selective to the target molecules. Among the chemicals for which analysis is needed, herbicides and pesticides residues are of importance due to their high toxicity and the risk they present for the environment and for human health. Sensor designs for the analysis of herbicides and pesticides were done by incorporating humic acid (HA) as the sensing layer to achieve the bio-recognition toward herbicides [33,34]. HA are organic macromolecules resulting from the microbiological decomposition of animals and plants. They are able to interact with metallic cations as well as herbicides. The formation of a complex is due to the presence of both oxygen rich functional groups such as carboxyl (COOH), carbonyl (C=O), hydroxyl (OH), and hydrophobic aliphatic and aromatic groups. HA has been mainly used in modified carbon paste on electrodes to tailor and improve their detection from aqueous solutions. Recent developments on the utilization of HA involved their layer-by-layer assembly into thin films which were used as a semi-permeable membrane and in electrochemical detection of pesticides [35,38].

Chemical detection of compounds such as ammonia is also of interest as it is produced in large quantity (2.1-8.1 Tg/year) by the chemical industries to be used as fertilizers and in refrigeration system [39]. Because of its toxicity, ammonia presents serious health hazards, and the monitoring of its concentration in air and liquid is of

major importance. Concentration control of ammonia not only interest environmental agencies but also, for example, the automotive industry as ammonia has been found in exhaust systems with concentrations up to 8 ppm [40,41]. There are also medical interests in measuring ammonia in the body as it can be an indicator of disorder or disease and for instance, breath ammonia level can be a diagnostic for urea imbalance as a result of kidney disorder or stomach bacterial infection [42,43].

Chemical sensors have been designed with detection limit lower than part per million (ppm) with fast response and good reproducibility. Sensors which have already been commercialized have a detection mechanisms often based on metal-oxide or organic conducting films, whose electrical properties are perturbed upon adsorption of ammonia molecules [44,45]. Films based on  $\text{SnO}_2$  or  $\text{WO}_3$  demonstrated good response to  $\text{NH}_3$  with a detection limit down to 1 ppm [46]. Films from conjugated polymers such as polypyrrole or polyaniline have also been used to detect ammonia by changing their conduction properties [45].

### *2.1.3 Nanoparticles as optical sensors*

Research on optical sensors based on nanotechnology has been widely developed and finds applications in the field of electronic nose and electronic tongue for quality control, environment monitoring or even safety such as chemical warfare or household safety. The properties of silver nanoparticles have been extensively studied in the past few decades for their unique optical, sensing and anti-microbial properties [48,48]. While Surface Enhance Raman Scattering (SERS) is probably the most spectacular application of silver nanoparticles, other sensing methods have been developed simply based on shifts in the spectral transmission of nanoparticles solutions. Solutions of spherical silver nanoparticles are known to have a strong yellow color and an extinction UV-Vis spectrum featuring a sharp peak at 400 nm [49,50]. The absorbance is caused by the localized surface plasmon absorption (LSPR) which arises from the coupled oscillations of the conduction electron in the metallic nanoparticles induced by the incident light electric field [51]. The position, shape and intensity of the



LSPR is function of factors such as morphology (size and shape), dielectric constant of the environment (coating, surrounding medium and supporting substrate) as well as inter-particle coupling (state of aggregation) [52]. Changes in LSPR position and intensity due to variation in surrounding medium's dielectric occur when either a solvent of different polarity surrounds the metallic nanoparticle or a molecule such as surfactant or polymer adsorb directly onto the nanoparticles surface [54]. Changes in nanoparticles proximity can be for example induced by DNA strands modified nanoparticles which leads to the aggregation of the particles upon multiple binding [53]. Changes in the shape of particles were also recently reported for the detection of mercury by gold nano-rods which morphology reversed to a more thermodynamically stable spherical shape [54]. Although nanoparticles solutions can have a very low detection limit, another approach for the fabrication of sensor is to use nanoparticles immobilized into thin films. While metallo-porphrins were used in electronic nose application [55], the nanoparticles sensing properties when assembled into thin films were evaluated only for gold and for a very limited set of solvent and chemical. Interaction between the solvent and the polyelectrolytes used in the layer-by-layer deposition was also not investigated. Metallic nano-thin films of silver were also reported by Rubner et al. but the targeted application was for the design of anti-microbial surface [56]. The sensing potential of nanoparticles embedded into a polymer matrix was reported but in this system, the swelling of the polymer matrix induced the decoupling of the nanoparticles and the color change.

## 2.2 Silver nanoparticles

### *2.2.1 Preparation of silver nanoparticles*

In the early 1900's, the emergences of the nanotechnology lead to a renewed interest in the preparation and characterization of metallic, inorganic and organic nanoparticles. A key point was the development of the scanning and transmission electron microscope (SEM and TEM) which allowed for the first time their direct visualization. Since then, a wide variety of methods has been developed for the

preparation of metallic nanoparticles including both top-down and bottom-up approaches. These two approaches describe two symmetrically opposed techniques to obtain nanoparticles and mainly differ from the starting material. A very simplified and cartoonist view of these processes would be that in the top-down approach, the trunk of a tree is used to fabricate a toothpick while in the bottom-up fibers of wood pulp would be pressed together to obtain the final toothpick. In the top-down approach, the starting materials can be macrosized bulk materials such as a gold foil or a piece of metal which the size is reduced by milling or attrition, laser ablation or lithography. These techniques usually produce particles which then to be bigger and with a broader size distribution. On the other hand, the bottom up approach, which is nowadays much more popular, utilize atoms and molecules as starting materials. These atoms or molecules are condensed into nanoparticles via liquid or gas phase homogeneous nucleation, heterogeneous nucleation on substrate or self assembly. Among all the methods used for the preparation of nanoparticles, the preparation in liquid phase has received growing interest due to its simplicity as it does not require any specialized instruments and can be performed in a beaker. The chemical reduction of precursor metallic salts is used for the preparation of narrow size distribution of metals such as silver, gold, copper, platinum, palladium nanoparticles. Numerous methods have been developed using different solvent systems such as water, ethanol, isopropanol, DMF and different reduction methods including  $\text{NaBH}_4$ , Hydrazine, sugar, UV, citrate, gamma-ray. All these parameters have been the subject of extensive publications and reviews [25-27]. Usually, when considering the preparation of metallic nanoparticles, the parameters used to consider are the solvent system, the reduction method and the capping/stabilization method. This preparation method is summarized in Figure 2.3 where a metallic ion with a valency  $n$  is dispersed in a solvent in the presence of a stabilizing agent. Upon reduction, the zero valency metal atoms ( $\text{M}^0$ ) aggregate into nanoparticles, which growth is controlled by the stabilizing agent.

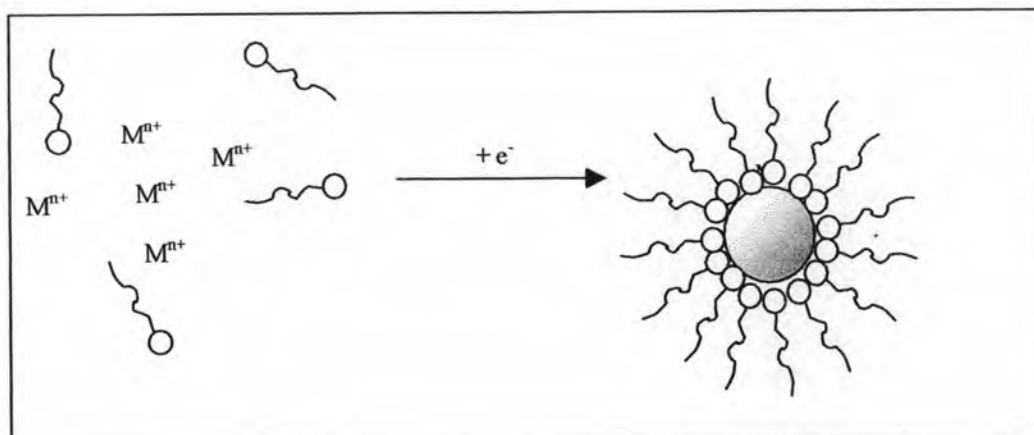
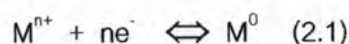


Figure 2.3: Diagram showing the reduction reaction of metallic ions into nanoparticles

### 2.2.2 Reduction of metallic salts

The basic reaction involving in the formation of a zero valent metallic atom is a reduction reaction during which electrons are transferred to the metal ions and could be generalized according to the following reaction:

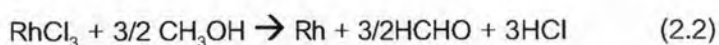


The formation of mono-sized metallic nanoparticles is usually achieved by mixing the metallic salt with a dilute solution of polymeric materials which then adhere onto the growth surface. The polymeric coating prevents the diffusion of metallic atom, the growth of the particle as well as preventing the coalescence of the particles by steric hindrance or electrostatic repulsion. The preparation bath usually contains three components which are the precursor salt, the capping agent and the reducing agent. The precursor salt composes of elemental metal, inorganic salts and metal complexes such as Ni, Co,  $HAuCl_4$ ,  $H_2PtCl_6$ ,  $RhCl_3$  and  $PdCl_2$ . Reduction agent include sodium citrate, Hydrogen peroxide, hydroxylamine hydrochloride, citric acid, carbon monoxide, phosphorus, hydrogen, formaldehyde, aqueous methanol and sodium hydroxide.

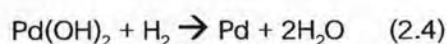
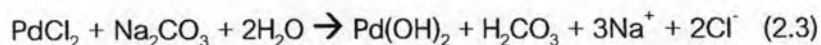
Colloidal gold is often prepared using a 50 years old method in which sodium citrate reduces chloroauric acid at  $100^{\circ}C$ . In a typical experiment, 20 ml of a  $2.5 \times 10^{-4} M$



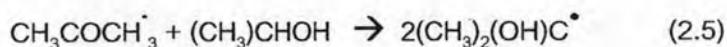
chloroauric acid is boiled while a 1 ml of a 0.5% sodium citrate is added. The solution is kept boiling until a deep red color develops signifying the presence of gold nanoparticles. The particles display an average 20 nm particle size and the solution is very stable. It has been demonstrated that a large number of nuclei leads to the formation of smaller particles. Hirai and coworker prepared colloidal rhodium by refluxing a solution of rhodium chloride and PVA in a mixture of methanol and water, 1:1 ratio, at 79°C. Methanol was used as the reducing agent and the reaction could be summarized as follows:



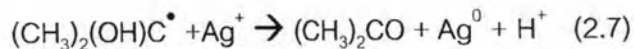
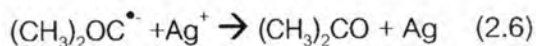
Hydrogen gas is also used a reducing agent in the preparation of nanoparticles. Rampino and Nord successfully prepared platinum and palladium nanoparticles using this technique. In this method precursor salts  $\text{K}_2\text{PtCl}_6$  and  $\text{PdCl}_2$  diluted in water were first hydrolyzed to form hydroxide prior to hydrogen reduction. Sodium carbonate was used to promote as a catalyst the hydrolysis reaction of palladium whereare sodium hydroxide was used for platinum hydrolysis. The following reactions were proposed:



Concerning the reduction of silver salts to silver nanoparticles, various methods have been developed and for example, Ag nanoparticles can be obtained by UV illumination of a  $\text{AgClO}_4$ , acetone and 2-propanol. UV irradiation produces ketyl radicals via excitation of the acetone and subsequent hydrogen atom abstraction from 2-propanol.



The ketyl radical may further undergo protolytic dissociation reaction. Both ketyl radical and radical anion react with reduced silver ions to form silver atom:



Capping agent includes polymeric materials such as polyvinylirolidone (PVP), poly(vinyl alcohol) (PVA) and acrylated polyelectrolytes. Non polymeric capping agent containing sodium citrate which can act both as reducing agent and stabilizing agent for gold nanoparticles preparationas also been used. Thiol bond (-SH) is also known to have a great affinity with gold and metallic surfaces which renders them to be useful the stabilization of nanoparticles in organic solvent.

### 2.2.3 Homogeneous nucleation growth

Upon reduction of the metallic ions, a supersaturated solution of metal atoms is formed. When the concentration of atom reached a critical value, homogeneous nucleation occurs leading to the formation of a new phase of metallic nanoparticles. The reduction in Gibbs free energy is the driving force for both nucleation and growth and occurs spontaneously if the solute concentration (C) is above a critical value  $C_0$ . When  $C > C_0$ ,  $\Delta G_v$  is negative and nucleation occurs spontaneously. Assuming a spherical nucleus with a radius of r, the change in Gibbs free energy or volume energy,  $\Delta\mu_v$  can be described by:

$$\Delta G_v = -kT/\Omega \ln(C/C_0) \quad (2.8) \quad \text{and} \quad \Delta\mu_v = 4/3 r^3 \Delta G_v \quad (2.9)$$

However, this energy  $\Delta G$  reduction is counterbalanced by the introduction of surface energy, accompanied with the formation of a new phase. This results in an increase in the surface energy,  $\Delta\mu_s$  of the system can be presented by the following equation where  $\gamma$  is the surface energy per unit area.

$$\Delta\mu_s = 4 \Pi r^2 \gamma \quad (2.10)$$

The total change of chemical potential for the formation of the nucleus,  $\Delta G$ , is given by

$$\Delta G = \Delta\mu_v + \Delta\mu_s = \frac{4}{3} r^3 \Delta G_v + 4 \pi r^2 \gamma \quad (2.11)$$

If  $r$  is smaller than a critical value  $r^*$ , the nucleus will not be stable and will dissolve back to reduce the overall free energy, whereas if the  $r > r^*$  then the nucleus is stable and will grow into nanoparticles. The critical size  $r^*$  is given by:

$$r^* = - 2 \gamma / \Delta G_v \quad (2.12)$$

In the preparation of nanoparticles by nucleation, this critical size is the limit on how small nanoparticles can be prepared. To reduce the critical size it is necessary to should increase the change in Gibbs free energy,  $\Delta G_v$  and reduce the surface energy of the new phase  $\gamma$ . It has been seen from previous equation that  $\Delta G_v$  can be increase by increasing the supersaturation  $C / C_0$ , temperature which can also influence the critical nucleus' radius as well as the type of solvent or the adjunction of surfactant.

#### 2.2.4 Stabilizing agent

Without the action of the stabilizing agent, the nanoparticles would grow into larger particles up to micron size by aggregation and Ostwald ripening. The role of the surfactant is to prevent the nanoparticle-nanoparticle interaction by steric hindrance or electrostatic repulsion preventing thus the coalescence and further growth of the nanoparticles. Numbers of surfactants have been used and are chosen as a function of the solvent. Dodecyl trimethyl-ammonium bromide (DTAB), cetyl trimethyl-ammonium bromide CTAB, citrate are commonly used in the preparation of silver nanoparticles. Although water soluble polymer poly(ethylene oxide) and poly(vinyl alcohol) have also been successfully used as stabilizing agent, polyelectrolytes containing acrylic functional groups such as (polymethacrylate) are also often used at stabilizing agent for the preparation of nanoparticles.

### 2.2.5 Optical properties of silver nanoparticle solutions

When noble metal nearly monodisperse spherical nanoparticles in solution are excited by electromagnetic radiation, they exhibit collective oscillations of their conduction electrons that result in wavelength selective absorption and scattering of the incident radiation. With colloidal silver nanoparticles, this excitation results in an extinction spectrum exhibiting a single peak around 400 nm known as the localized surface plasmon resonance (LSPR) [57] and can be seen on Figure 2.4. Based on the work of Gustav Mie's in the early 1900's, it has been known that the various colors that colloidal gold solutions can display (and hence the shifts of the LSPR) are dependent on the particle size and shape [58,59].

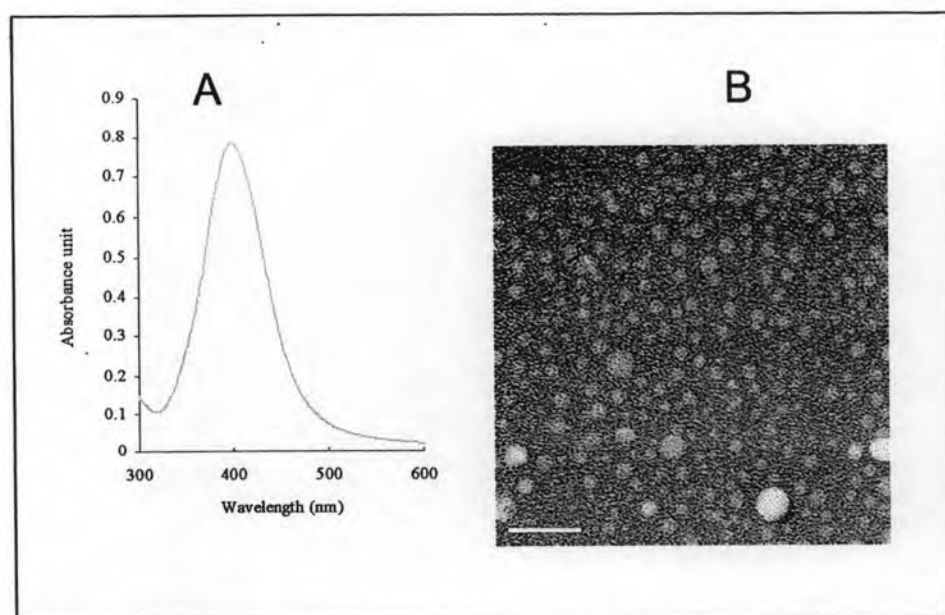


Figure 2.4: (A) UV-Vis spectrum of silver nanoparticles and (B) transmission electron microscopy image of the nanoparticles. The scale bar on the TEM image represent 20 nm.

This property of colloidal solutions to display changes in the visible spectrum was extensively applied in the development of sandwich immunoassays [60-62]. The change in size and shape of antibody-gold nanoparticles conjugates occurring when

their agglutination was induced by the presence of the antigen resulted in a dose-dependent decrease in extinction of the LSPR of the gold colloid. This new immunoassay method showed promise since the technique was homogeneous, i.e., did not need a separation of the free antigen from bound complexes. Unfortunately, the LSPR effect proved very sensitive to non-specific interactions and was barely applicable to crude serum or urine samples [63]. However when a suitable separation of the possible interfering components in the sample could be effected, the technique proved useful as shown later by its application to the determination of the affinity of monoclonal antibodies [64]. The technique is also applicable to the study of oligonucleotide hybridization in buffered solutions [65]. Besides the effects of size and shape on the LSPR of noble metal colloids which were demonstrated [66], the effect of changes in the refractive index of the surrounding medium was more difficult to appreciate at an experimental point of view because of the very high susceptibility of the nanoparticles to flocculate in organic compounds. The direct effect of the refractive index of the surrounding medium was actually demonstrated with gold colloids in 1994 [67] with gold and silver colloids in 1995 [68] and confirmed more recently with silver nanoparticles [70]. Gold spherical nanoparticles obey the physical laws of any particle of a size smaller than that of the incident light [71] and therefore, their extinction at a given wavelength  $E(\lambda)$  is the sum of absorbance  $A$  and scattering  $S$  for a given optical pathlength  $L_t$ , according to the relationship:

$$E(\lambda)L_t = S(\lambda) + A(\lambda)L_t \quad (2.13)$$

The Mie scattering treatment for metal particles allows to relate the extinction term to the refractive index of the surrounding medium by a tedious expansion of complex series of scattering coefficients that describe the amplitudes of the scattered and magnetic fields. The Maxwell–Garnett approach is easier to handle [72], which assumes that it is reasonable to define an effective complex dielectric constant  $\epsilon_m$  for the metal particles and a complex dielectric constant  $\epsilon_0$  for the medium that surrounds



them. These constants are related to the particle polarizability  $\alpha(\nu)$  by the Lorentz–Lorentz relation:

$$\alpha(\nu) = f_m \left( \frac{\epsilon_m - \epsilon_0}{\epsilon_m + \kappa \epsilon_0} \right) \quad (2.14)$$

Where  $f_m$  is the volume fraction of the metal in the mixture and  $\kappa$  is the screening parameter depending on the geometry of the metal inclusions ( $\kappa = 2$  for spheres and tends to unity for needles oriented with their axes of revolution parallel to the direction of incident light). The complex dielectric constant of the metal  $\epsilon_m$  can be calculated by assuming a Drude model as:

$$\epsilon_m = \epsilon_m^\infty - \frac{\omega_p^2}{\omega(\omega + i\omega_\tau)} = \epsilon'_m + i\epsilon''_m \quad (2.15)$$

where  $\epsilon_m^\infty$  is the dielectric constant contribution from bound electrons,  $\omega_p$  is the plasmon frequency and  $\omega_\tau$  the damping frequency of the bulk metal, and  $\omega$  the angular frequency of the incident light as defined above. The complex dielectric constant can further be decomposed into its real and imaginary components  $\epsilon'_m$  and  $\epsilon''_m$ , respectively. The optical extinction cross section  $C_{E(\lambda)}$  for a single particle is related to the particle polarizability  $\alpha(\nu)$  via its absorbance and scattering cross sections as follows:

$$C_{E(\lambda)} = k i \alpha(\nu) + \frac{k^4}{6\pi} |\alpha(\nu)|^2 \quad (2.16)$$

where

$$k = \frac{2\pi r \sqrt{\epsilon_0}}{\lambda} \quad (2.17)$$

in which  $r$  is the particle radius.

Finally, the transmittance  $T$  is related to the extinction cross-section by the following relationship, where  $N$  is the number density of particles.

$$T = e^{-NC_{E(\lambda)}L} \quad (2.18)$$

In the case of noble metals, as exemplified for gold, in the visible region of the spectrum shows that the imaginary part of the complex dielectric constant  $\epsilon_m$  is small and does not vary with  $\lambda$ , counter to the real part which is negative and decreases monotonically with  $\lambda$ . Therefore, if we consider only the real part of  $\epsilon_m$  and  $\epsilon_0$ ,  $\alpha(\nu)$  and hence  $C_{E(\lambda)}$  will become very large when  $\epsilon'_m + \kappa \epsilon_0 \rightarrow 0$ , i.e., at the wavelength corresponding to the LSPR of the metal. As a consequence, any tiny change in the complex dielectric constant and hence in the refractive index ( $n_0 = \sqrt{\epsilon_0}$ ) of the surrounding medium will change the wavelength of the LSPR. This principle is applied in the SPR measurements with colloidal gold.

### 2.2.6 Effect of particle size on the plasmon absorbance

One of the main variables in the preparation of metallic nanoparticles is their size distribution. Processes have been developed in order to decrease the mean size and the poly-dispersity in size. This means that the objective is to obtain smaller particles and which have all the same diameter. Although intuitively one might expect the plasmon resonance band to be strongly dependent on the particles size, it is in fact not the case. By looking carefully at the theoretical expression of the extinction coefficient of the nanoparticles, one can see that the particles size is not a variable in the equation of  $C_{ext}$ . This means that the position of the plasmon band is independent of the nanoparticles size as it can be seen in the following Figure 2.5. Although this fact is true for small particles with a diameter smaller than 50nm, if the particle size exceed this limit a red shift as well as a decrease in plasmon absorbance amplitude can be observed.

This decrease in absorbance will continue until the particle size reach 100 nm after which the solution become transparent and the plasmon band has disappeared.

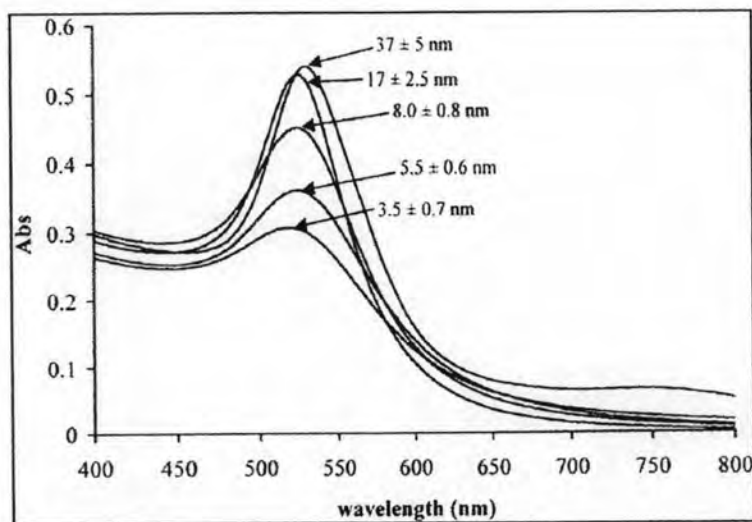


Figure 2.5: Effect of the particles size of the gold nanoparticles on the UV-Vis absorbance spectra.

### 2.2.7 Effect of changes in dielectric of the surrounding

From theoretical consideration, the extinction coefficient is directly dependant on the dielectric of the surrounding medium. Because resonance frequency of the dipole formed by the electron plasmon oscillation is sensitive to the surrounding electrostatic polarizability, any changes in solvent quality on the surrounding of the nanoparticles will induce a change in plasmon band position. Theoretical calculation shown hereafter predicts a plasmon shift which has a linear dependence with the dielectric of the surrounding medium. In Figure 2.6 it can be seen that when the solvent polarity is decreased from 1.7 (toluene) down to 1 (air), the plasmon band maximum absorbance shifts from 775 nm to 675 nm. This mechanism can be understood by the fact that a solvent with a higher refractive index will also have a lower polarizability which in turn will decrease the interaction between the electron plasmon and the surrounding medium. Lower level of electrostatic interaction also suggests lower resonating frequency and therefore higher lambda with a red shifted LSPR.

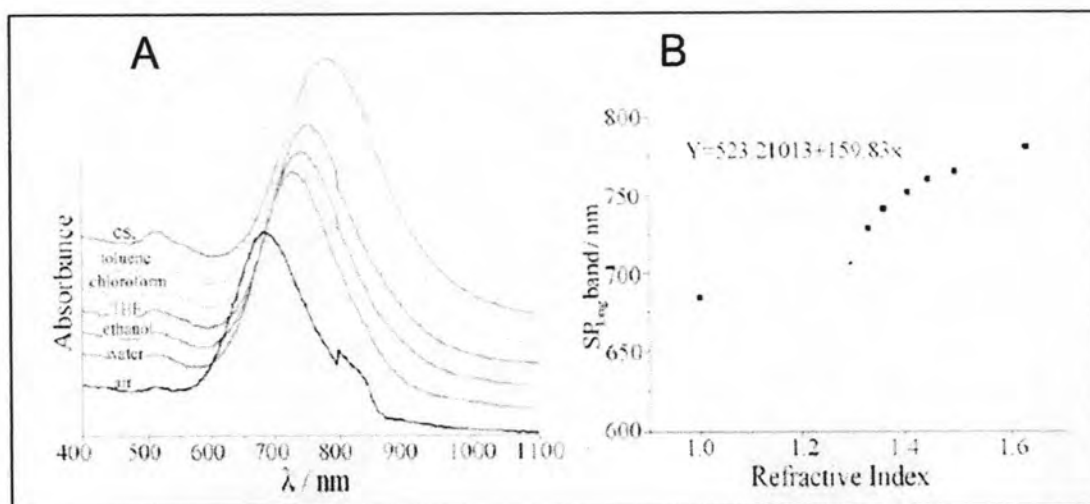


Figure 2.6: (A) UV-Vis spectra of gold nanoparticles when exposed to various solvents and (B) plot of the changes in the value of the lambda max as a function of the refractive index of the nanoparticles surrounding.

### 2.2.8 Effect of changes in capping thickness

Another parameter which can perturb the optical properties of silver nanoparticles solution is the type of capping used to stabilize the nanoparticles. When nanoparticles are modified in order to improve their stability in solvent or functionalize for sensing applications, the capping layer itself perturb the plasmon resonance of the nanoparticles. This has for effect to shift the plasmon peak as it can be seen in Figure 2.7 toward higher wavelength. The magnitude of the shift is function of the thickness of the applied layer and is red shifted when the PMMA layer thickness is increase. Shown here is the application of a 16 nm capping layer which has for effect to shift the plasmon band maximum absorbance from 360 nm to 420 nm.

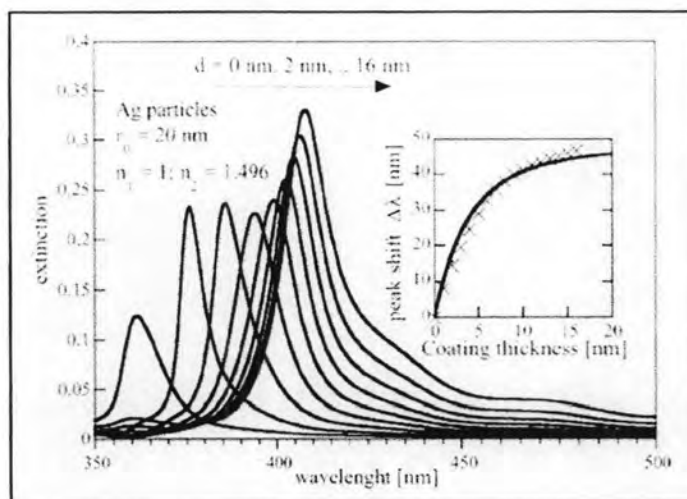


Figure 2.7: Effect of changes on coating thickness of stabilizing agent of the nanoparticles on the value of the lambda max UV-Vis absorbance.

### 2.2.9 Coupling of nanoparticles and interparticle interaction

Probably the most used optical properties of metallic nanoparticles is their interparticle interaction. When a particle is isolated it interacts individually with the surrounding media and the incoming electromagnetic vibration of the incident light. The frequency of resulting dipole is then function of the parameter discussed earlier. When a second nanoparticle, having its own dipole, is positioned near the first nanoparticle, the two dipoles are going to interact and influence each other. The minimum distance between the two particles for the interaction to occur has been calculated to be the diameter of 3 nanoparticles combined. This type of interaction is described as coupling interaction and is useful for nanoparticles sensing of very dilute analyte in solution down to PPM or PPB. To this end the nanoparticles are usually modified with a coating which has some strong affinity for the analyte. The binding of the analyte with the nanoparticles will induce the two nanoparticles to get closer and eventually their respective plasmon band will be shift due to the coupling interaction.



## 2.3 Layer-by-layer formation of polyelectrolyte multilayers

### 2.3.1 Principle of polyelectrolyte multilayer assembly

A polyelectrolyte multilayer (PEM) is a monolayer polymer thin film of a polyelectrolyte assembled using the a layer-by-layer deposition method. This technique, first reported by Decher [76-77] was initially based on the sequential complexation of polyanionics and polycationics species at a substrate interface. This technique developed in the early 90's came as a supplement of previously used methods for the preparation of thin films such as spin coating of polymer solution, thiol modification of gold as well as langmuir-blodget thin film. The PEM technique in the last decade has emerged as an alternative method for the preparation of multilayer thin films (and is getting more popular everyday) mainly due to the versatility of the assembly technique, the ease of preparation and the low cost of chemicals used. The versatility comes from the fact that a very wide range of chemical and nanostructures can be assembled using this technique. The ease of preparation is due to the fact that the deposition process is controlled by a simple dipping process and only requires beakers. The inexpensiveness is function of the type of structures built but commonly used polyelectrolytes such as PDADMAC or PSS are inexpensive furthermore and the concentration used are often in mM which make the chemical consumption very low [78,82]. This dipping process is summarized in Figure 2.8 where the different dipping steps can be seen. A bare substrate after being cleaned of any organic contaminant is dipped in a solution of cationic polyelectrolytes followed by 3 rinse steps. The surface of the substrate is therefore reversed from the initial negatively to oppositely charge which then allow for the deposition of anionic polyelectrolytes again followed by 3 rinses. These steps lead to the formation of a bi-layer. These dipping steps can be repeated as many times as desired and lead to the formation of a multilayer coating which thickness can be tuned by the number of dipping cycles. The surface and bulk propertied will be tuned by the type of component used in the deposition process and can include nanoparticles [108,111], biomolecules [96-100], conducting polymer [94] or even photoactive chemicals [95].

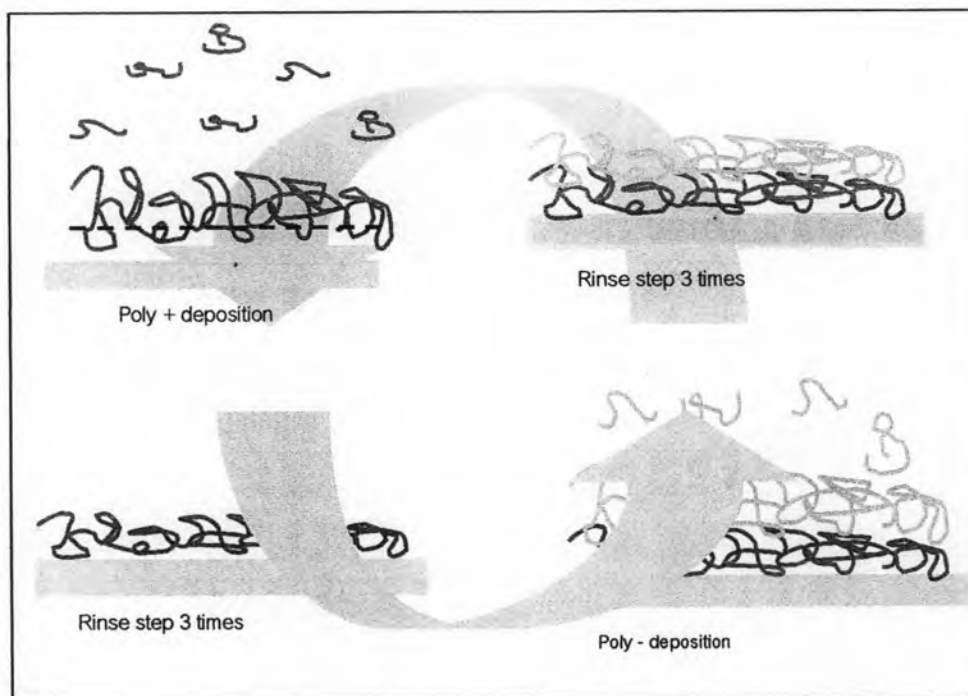


Figure 2.8: diagram depicting the deposition steps used in the preparation of polyelectrolytes multilayers.

The driving force for the adsorption of a charged polyelectrolyte onto an oppositely charged surface is due to the electrostatic interaction between oppositely charged polyelectrolytes. The complexation is known to be entropically driven and results in the release of a pair of counterions. Using micro-calorimetry, Zjhe and Schlenoff [138] have shown that the complexation reaction is a highly favorable process which is strongly dependant of the ionic strength of the polyelectrolyte solution. The complexation of polyelectrolyte has been extensively studied in the early 1900 yet and the theoretical, experimental and computational knowledge are quite uneven. While experimental measurement of the behaviors of polyelectrolytes complexes in solution are fairly easy to study, their behavior is more difficult to explain on a theoretical as well as computational point of view. The large size of macromolecules and long polymer chains are difficult to compute and requires extensive calculation time. In order to reduce the calculation time, polyelectrolytes are often modeled by chain assembly of charged beads linked by springs [84, 87]. Similar modelisation difficulties have been seen in PEM thin film growth when researcher tried to find theoretical justification to the

phenomenon observed. Although excellent work from Joanny et al, Kotov and Schlenoff [84,85,88] to name a few, has been published, it is still difficult to predict the properties of a thin film based on the type of polyelectrolytes used in the assembly and based on the type of structures chosen including experimental conditions. On the experimental side, the major parameters controlling the growth of a PEM have been identified as ionic strength of the solution, the type of functional groups present on the polymer backbone and the linear charge density of the polymer which is function of the pH of the solution [78-82]. The final thickness of a PEM can be finely tuned by controlling each of these parameters as well as the number of deposited layers. By finely tuning the deposition conditions, the bulk and surface properties can be controlled as a function of the desired application.

The simple dipping steps used in the layer-by-layer deposition of oppositely charged polyelectrolytes can be extended to a variety of constituent including biopolymer, conducting polymer, protein, enzyme or even inorganic, organic and metallic nanoparticles. Several reviews have summarized the range of application developed based on the layer-by-layer technique. These include light emitting or light harvesting devices, fuel cell, biomedical applications with biocompatible surface, cytophobic / cytophobic surface and tissue engineering by enhancement of cell adhesion and proliferation. PEM films have also been used in a wide range of sensor and biosensors based on the immobilization of enzyme, electro active species and nanoparticles.

### *2.3.2 Type of polyelectrolytes*

A polyelectrolyte is a polymer consisting of monomers with a negative charged anion (polyanion), a positive charged cation (polycation) or both positive and negative polyampholyte. Some examples of such polyelectrolytes are shown in Figure 2.9. Due to the presence of ionic functional groups on their monomers, polyelectrolytes exhibit the characteristic to be water soluble. The presence of charge species on the backbone of the polyelectrolyte do not always guarantee the solubility in water and for example when

the charge density of a pH dependant polyelectrolyte decrease below a critical value the polyelectrolyte will precipitate (e.g. PAA). As a rule, the polyelectrolyte behavior can be expected if more than 1 ionic site per 10 monomeric units is present in a polyelectrolyte [85]. Also depending on the nature of the monomer used, some polyelectrolytes are only soluble in organic solvents (PNO4VPI) while some polyelectrolytes are soluble in both water and organic solvent. When compare with their neutral counterpart, polyelectrolytes present different properties in solution mainly due to their conformational dependence to the ionic strength of the solution. In absence of salt, polyelectrolytes present an extended and stretched structure due to the repulsion of similar charges present on the backbone of the polymer. When salts such NaCl are added in the solution, the electrostatic repulsion is screened by the counterions and leads to a collapsed and coiled structure.

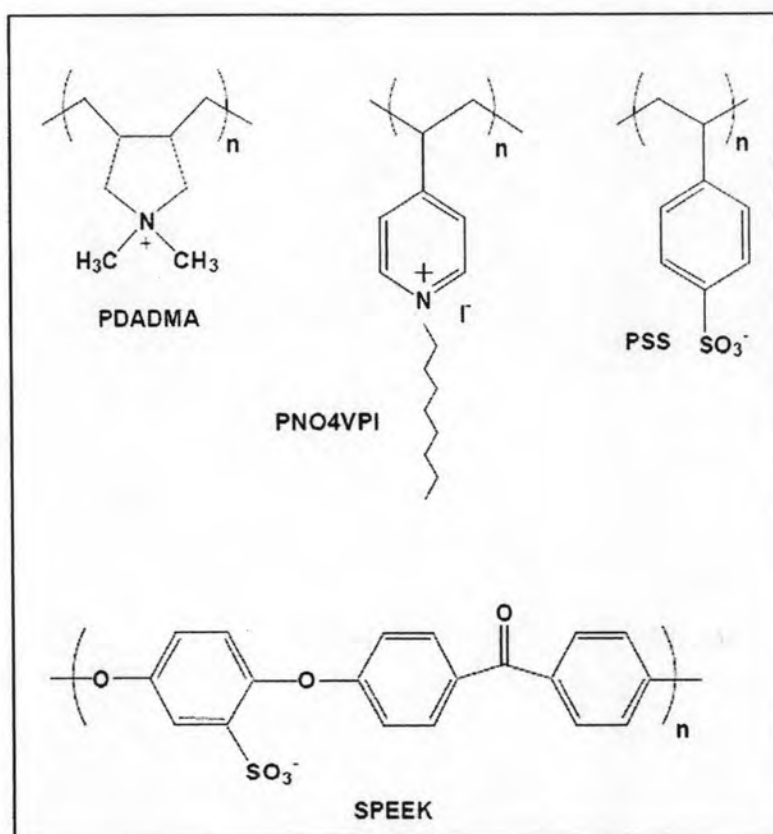


Figure 2.9: Chemical structure of some typical polyelectrolytes



The synthesis of polyelectrolyte is similar to that of common polymers. These include free radical polymerization in homogenous and heterogeneous phase, ionic polymerization as well as polycondensation and polyaddition. The polyelectrolyte can be synthesized as homopolymer, copolymer or block copolymer based on the reaction of a mixture of monomer and for example poly(styrene sulfonate)<sub>0.66</sub>-co-poly(maleic sodium salt)<sub>0.33</sub>. One interesting point with polyelectrolytes is that in contrast with the huge variability of the polymer backbone structure, the number of different chemical structures of anionic or cationic sites responsible for the peculiar behavior of the polyelectrolytes in solution is rather small. The most commonly encountered cationic groups include  $-\text{NH}^{3+}$ ,  $=\text{NH}^{2+}$ ,  $\equiv\text{NH}^+$  and  $-\text{NR}^{3+}$  and the anionic groups include  $-\text{COO}^-$ ,  $\text{CSS}^-$ ,  $\text{SO}_3^-$  and  $\text{OPO}_3^{2-}$ .

### 2.3.3 Polyelectrolyte in solution

As mentioned earlier, in contrast with the well established theory of uncharged polymer in solution, the knowledge on the behavior of polyelectrolyte is poor. It is the electrostatic nature of the polyelectrolyte which renders their theory much more complex to understand and computational simulations are much more expensive and require long CPU time when compare with neutral polymers. Whereas excluded volumes are the only important interaction in uncharged polymer, the long range coulomb interactions induce new parameters and particularly the effect of the ionic strength of the solution on the conformation of the polyelectrolyte [83, 86].

Polyelectrolytes can be seen as a chain of  $N$  monomers of size  $a$ , with a fraction  $f$  of which are charged. The parameter  $f$  represents the linear charge density of the polymer which can be fixed of function of the pH of the solution. If the charge is very low, the electrostatic interaction do not play an important role and the chain is Gaussian with and end to end distance  $R_0 = N^{1/2}a$ . If the charge is higher, the polymer chain is elongated and stretch by the electrostatic repulsion of same charge monomers. The repulsion of each monomer can be decreased by adjunction of salt (NaCl) in the



solution which tends to screen the repulsive force and allow more flexibility to the polyelectrolyte chain. If a concentration  $n$  of salt is added to the solution the columbic interaction between two charges at a distance  $r$  is given by the debye-huckel potential  $V(r)$  where  $l_B$  is the Debye length and  $\kappa$  the inverse Debye length.

$$V(r) = kT l_B / r \exp(-\kappa r) \quad (2.20)$$

$$l_B = q^2 / 4\pi\epsilon\kappa T \quad (2.21)$$

$$\kappa^{-1} = (8\pi n l_B)^{-1/2} \quad (2.22)$$

If no salt is added the chains are stretched and their size is expressed by  $R$  but if we use a weakly charged polyelectrolyte can be seen as an elongated chain of Gaussian electrostatic blobs with a size  $\xi_{el}$  containing each  $(f l_B/a)^{2/3}$  monomers

$$R \sim N_a (f l_B^2/a)^{1/3} \quad (2.23)$$

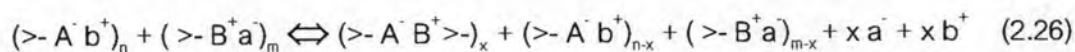
$$\xi_{el} = a (f l_B/a)^{-1/3} \quad (2.24)$$

The size of the blob is such that the electrostatic interaction inside are of the order of the thermal energy  $kT$ . When salt is added the chain start to bend and following the changes in persistent length  $l_p$  being is the length over which the chain remain stretch. The persistent length decreases with the salt concentration as  $\kappa^{-1}$  or  $\kappa^{-2}$ . At very high ionic strength the electrostatic are short range and is equivalent to an excluded volume  $v_{el}$ .

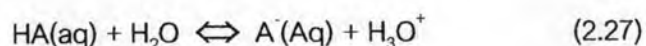
$$v_{el} = 4\pi l_B^2 f^2 / \kappa^2 \quad (2.25)$$

### 2.3.4 Polyelectrolyte complex

When 2 oppositely charged polyelectrolytes are mixed together in solution, a polyelectrolyte complex occurs and the solution becomes turbid. The polyelectrolyte complex can be insoluble if the polyelectrolytes are mixed in stoichiometric proportion or soluble if mixed in non stoichiometric proportion. The complexation reaction can be seen as reaction between an anionic polyelectrolyte  $A^-$  carrying a cationic counter ion  $b^+$  and a cationic polyelectrolyte  $B^+$  carrying an anionic counter ion  $a^-$ . The complexation reaction of  $x$  monomer leads to the formation of  $x$  complex and the release of as many counter ions salts. The degree of conversion can be defined as  $\Theta = x/m$ . The pH of the solution when using weak polyelectrolytes can be used to control the  $\Theta$  value.



The percent ionization of a weak polyelectrolyte is a function of pH but displays a behavior which is quite different from classical weak acid or weak base. When we write the dissociation of let say a weak acid the Arrhenius acid definition is based on the chemical equilibrium such as:



We can use the position of this equilibrium as a quantitative measure of the strength of an acid. The equilibrium constant is called the acid dissociation constant  $K_a$ :

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{and} \quad pK_a = -\log_{10}(K_a) \quad (2.28)$$

This dissociation constant is not an absolute number and varies as a function of temperature and the chemical environment. Among the parameters which influence the value of the pKa is the interaction with surrounding complexing agent. For instance when a carboxylic group which has a pKa of 4.4 is in presence of either favorable or unfavorable electrostatic interaction, its pKa will shift to higher or lower values. In

polyelectrolyte complex systems as well as in polyelectrolyte multilayers weak acid or base are associated through electrostatic interaction by complexation reaction shown earlier. This suggests that a carboxylate ( $\text{COO}^-$ ) functional group will become a carboxylic  $\text{COOH}$  more favorably than its complexed counterpart at pH near  $\text{pK}_a$  values. Recent work from Schlenoff [139] brought some light in the quantification of the change in  $\text{pK}_a$  values as a function of the type of polyelectrolyte complex formed inside polyelectrolyte multilayers using the UV-Vis absorbance shift of a poly-AZO compound. In their work they used a dye which has a  $\text{pK}_a$  value of 3.3. When exposing the dye to pH variation both free in solution or complexed into multilayers they were able to show that the  $\text{pK}_a$  value of the dye was decreased from 3.3 to 2.7 and 2.2 when immobilized into multilayer. The stabilization of the dye by complexation with PDADMAC which is a quaternary amine is used to explain the increased stability against protonation of the carboxylate groups. The implication of this work is that weak polyacid and polybase can be expected to display more acidic and basic character respectively and therefore would retain their ionic character in the polymer film. This point is an advantage and for example, chitosan which has a  $\text{pK}_a$  of 6.4 and should be neutralized above pH 7 display electrostatic affinities with anionic polyelectrolytes up to pH 8.

### *2.3.5 Formation of polyelectrolyte multilayers*

The formation of polyelectrolyte multilayers has been explained by the decrease in free energy due to the release of counterions leading to an increase in entropy. The release of hydration water upon complexation is also to be taken account for in making the complexation thermodynamically favorable. The complexation phenomenon is known to be virtually athermal and the cooperative association of oppositely charged segment to the formation of a tightly bounded network of polymer. Upon complexation, electrostatic neutrality of the multilayers is maintained by the formation ion pairs. No excess salt are left trapped in the multilayer film as it has been demonstrated in previous work using radio-labeled ions. The complexation mechanism can be defined as competitive ion pairing between oppositely charged polyelectrolytes segments and

counterions. While electro-neutralization is the dominant mechanism which can be brought into place by polymer neutralization of excess counterions added in solution which chemical potential can induce swelling of the film and infiltration of ions in the bulk polyelectrolyte complex. In the case of complexation between oppositely charge polyelectrolytes we talk about intrinsic compensation and extrinsic compensation when counterions are involved in the neutralization process. The competitive ion pairing mechanism can be described in Figure 2.10.

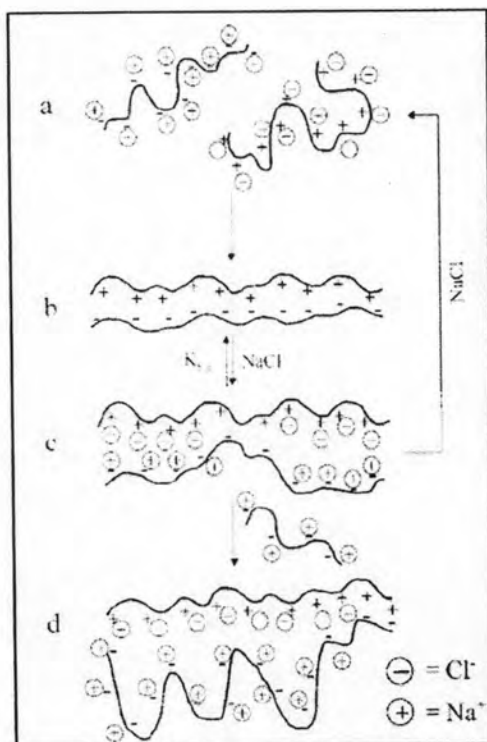


Figure 2.10: Diagram showing the swelling of polyelectrolyte complexes upon adjunction of NaCl.

### 2.3.6 Parameter controlling layer-by-layer growth

#### 2.3.6.1 Number of layers

One of the simplest methods for the control of the growth of multilayered thin film is to vary the number of layers. In this case the main parameters which are the type of

polyelectrolyte, the ionic strength of the solution, the concentration of the polyelectrolyte and the dipping time are kept constant. Shown in the following Figure is the relationship between thickness and number of deposited layers. It can be seen that after the deposition of few layers (6-8) the increase in thickness is constant for each deposition step because the amount of polyelectrolyte being deposited for each dipping cycle is constant. The step increment is function of the system parameters (salt, time, concentration and PE) and is constant if the system parameters are kept constant. This provides a very convenient method to control the thickness of the film with a nanometer resolution. In the Figure 2.11 thickness as a function of the number of layers for a PSS/PDADMAC multilayer deposited on silicon wafer from 1.0 M NaCl<sub>(aq)</sub> is depicted. Odd layers are from PDADMAC and even layers from PSS.

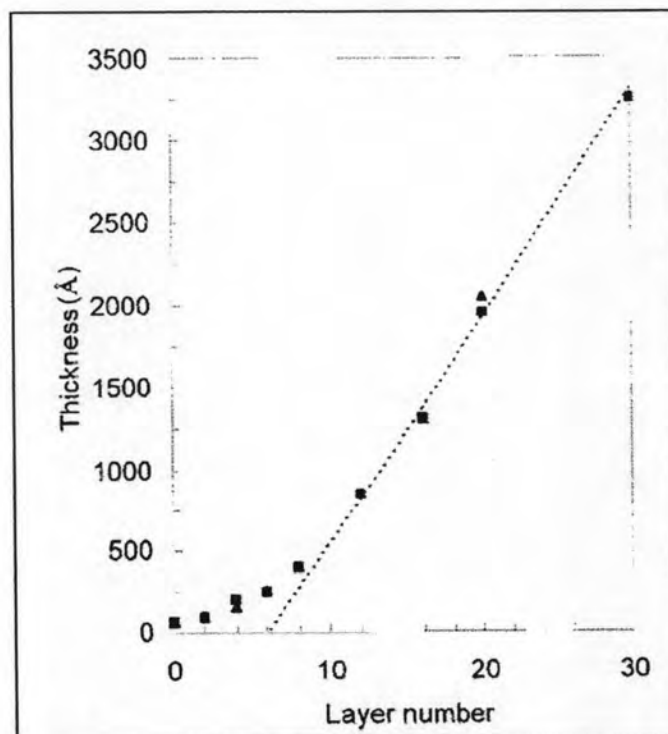


Figure 2.11: relationship between thickness and number of layer for a PSS/PDADMAC multilayer.



### 2.3.6.2 Dipping time and polyelectrolyte concentration

Another parameter which can be used to control the growth of multilayers is the dipping time and is shown in Figure 2.12. Because the adsorption of polyelectrolyte at the thin film water interface is controlled by a diffusion process time plays a major role in the formation of the multilayer. When the negatively charged surface is dipped in a positively charge polyelectrolyte, the electrostatic interaction are sufficient to allow a complex to be formed between the polyelectrolyte on the surface and the oppositely charged polyelectrolyte in solution. While the deposition occur, the surface charge become less negative and more positive as more polycationic polyelectrolyte adsorb onto the surface. When the surface is completely coated with the polycationic polyelectrolyte the adsorption of new polyelectrolyte is stopped due to electrostatic repulsion. This mechanism is described as self limiting adsorption process and is a major characteristic of the polyelectrolyte multilayers assembly.

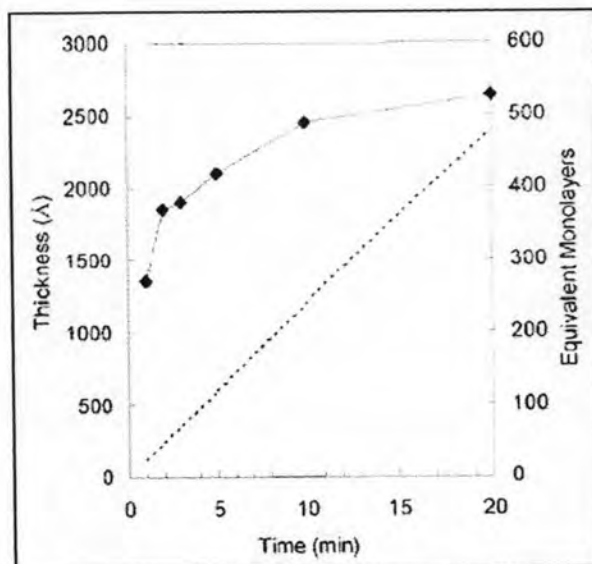


Figure 2.12: relationship between thickness and dipping timer for a PSS/PDADMAC multilayer

The kinetic of formation suggested by the previous experiment was further detailed using quartz crystal microbalance, UV-Vis spectroscopy, FTIR or optical waveguide lightmode spectroscopy (OWLS). The adsorption of charges molecules onto an oppositely charged surface is mostly controlled by diffusion which limits the number of molecules arriving at the interface and it is clear that higher concentration should induce faster deposition kinetic. Other parameters such as the ionic strength of the solution play a major role on the adsorption kinetic. Higher salt concentration tends to decrease the electrostatic interaction between polyelectrolyte and therefore decrease the repulsion at the surface which in turn increases both the kinetic and the maximum loading of polyelectrolyte onto the film. It can be seen from Figure 2.13 that a 0.1 mM polyelectrolyte concentration is sufficient for nearly maximum thickness of the final film.

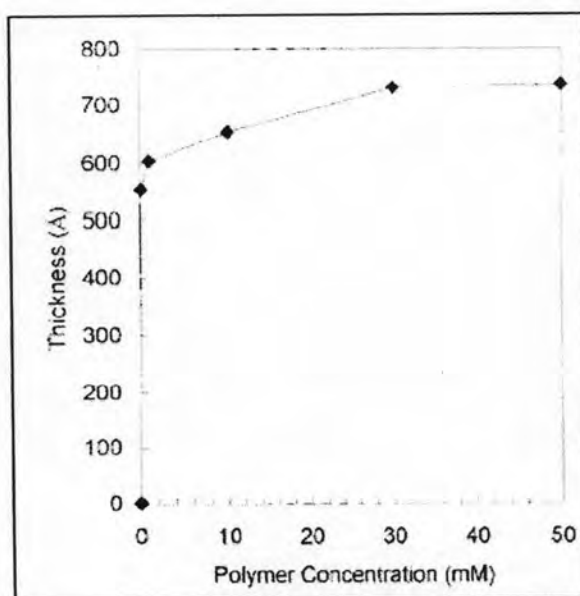


Figure 2.13: Relationship between thickness and polyelectrolyte concentration for a PSS/PDADMAC multilayer

### 2.3.6.3 Ionic strength of the solution

The last major parameter used to control the thickness of a film assembled using the layer-by-layer deposition of polyelectrolytes multilayers is the ionic strength of the solution. Schlenoff et al reported the linear relationship between thickness and NaCl concentration (Figure 2.14). The effect of the NaCl is triple as it act on the conformation of the polyelectrolytes in solution, on the electrostatic interaction between polyelectrolytes in solution and the surface and finally on the electrostatic interactions within the PEM film. The first effect of the conformation of the polyelectrolytes in solution has already been discussed and it is known that high salt concentration induce a coiling of the polymer chains by screening of the electrostatic charges on the polyelectrolytes. The second effect is also due to the screening of the electrostatic repulsion during adsorption onto the substrate, which induce a higher loading and diffusion rate of the polyelectrolytes onto the substrate. Finally the third effect of the ionic strength is to swell the film by competitive interaction with the polyelectrolytes- polyelectrolytes bound through the extrinsic compensation discussed earlier. The swelling of the PEM matrix leads to a looser network and allow the diffusion of polyelectrolytes chains inside the film. Evidence of interpenetration have been given by low angle X-ray diffraction showing no Bragg diffraction patterns which signify that there is no stratification in the film. Schlenoff et al. developed a model in which the penetration length  $l_{cp}$  is found to be linearly dependant with the ionic strength of the solution.

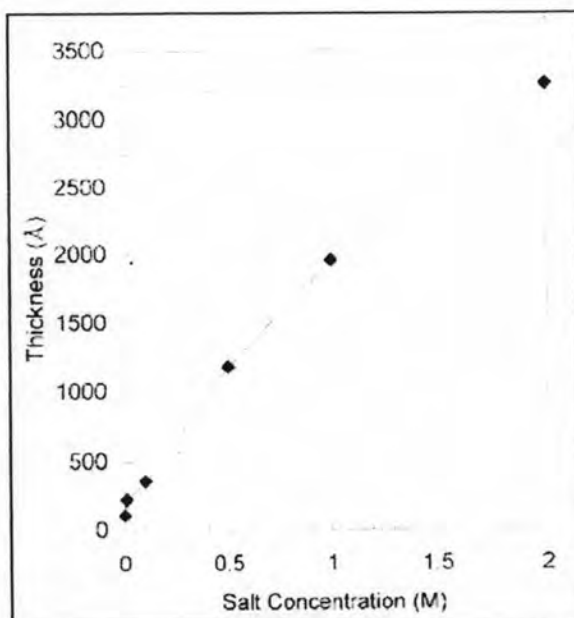


Figure 2.14: relationship between thickness and ionic strength of the polyelectrolyte solution for a PSS/PDADMAC multilayer

In conclusion, the major parameters controlling the formation of polyelectrolyte multilayers for a given polyelectrolyte pair are: ionic strength of the polyelectrolyte solutions, number of layers, deposition time and polyelectrolyte concentration. They can be varied and optimized in order to achieve maximum kinetic, maximum loading or maximum thickness of the final film. Good control over these parameters allow the scientist to build thin film with desired thickness as well as bulk and surface properties. Nevertheless, it is interesting to note that the sets of parameters used for the assembly are specific for each polyelectrolyte pair and cannot be generalized for each polyelectrolyte pair. For example a polyelectrolyte thin film assembled from PDADMAC and PSS has a maximum thickness when the ionic strength is increased at 2 M NaCl but if the PSS is substituted to PAA then the optimum ionic strength of the solution is 0.3 M. Similarly, for polyelectrolyte the optimum concentration is near 5 mM but when using smaller molecules the optimum concentration is 0.01 mM. These sets of parameters needed to be tediously reevaluated for every new polyelectrolyte pair.

## 2.4 Polyelectrolyte multilayers nanocomposite

### 2.4.1 Silver nanoparticles assembled into thin films

When the layer-by-layer technique was developed by Decher, the first publications involved only oppositely charged polyelectrolytes. When researcher interest on PEM film increased, more complex structures appear, PEM started to incorporate protein, conducting polymer and nanoparticles [125-137]. Among the first report of the layer-by-layer assembly of nanoparticles was made by Kotov *et al.* [126] in 1995. They first reported the successful assembly of PDADMAC and CdS nanoparticles into thin films. Using spectroscopic and microscopic technique as well photocurrent measurements they were able to confirm the assembly and stability of the composite film which also displayed interesting electro-luminescent properties. Early report of the layer-by-layer assembly of metallic nanoparticles was made [108,109]. They used the self assembly of gold nanoparticle and insulator layers to tune the electrical properties of thin films. Liz-Marzan and Mulvaney [134] also published some very interesting work in 2001 in which they showed that the optical properties of nanocomposite thin films can be tuned by controlling the packing density of the nanoparticles. In their experiments they used gold nanoparticles coated with increasing thickness of silica. Plasmon shifts due to interparticles interaction were observed as a function of the spacing of the nanoparticles in the film. Further control of the optical properties of nanoparticles thin films was introduced by Kotov and Liz-Marzan [131] who used the intercalation of clay nanoparticles to act as a spacing layer and reduce the interparticles interaction. Their results showed that the intercalation of a single layer of clay in between each gold nanoparticle layer was sufficient to suppress the plasmon band due to interparticles interaction in the UV-Vis spectra of the films. Metallic nanoparticles thin films were first reported for sensing application by Tsukruk *et al.* [115, 125] in their articles published in *Nature materials*. The coating of sacrificial membrane allowed for the design of new chemical and pressure sensors based on the optical properties of free standing gold nanoparticles membrane. Optimization of the nanoparticles size to be used in LbL



assembly for biosensing was proposed by Nath and Chilkoti [127]. More recently, tactile sensors have been developed by combining metal and semiconductor nanoparticles, nanocomposite thin films. The electro-optical properties of the film were found to be altered when pressure was applied onto the film. When coupled to a CCD camera, this design was shown to detect pressure distribution by converting changes in distance between nanoparticles into luminescence. Further development of distance controlled optical response of nanocomposite film suggest that more attention need to be given to the architecture used in the nanoparticle assembly.

The common point all published work on nanoparticle assembly rely on the use of the proper surfactant or stabilizing agent in the preparation of the nanoparticles in order to allow for their deposition into thin films. Although the deposition process is extremely simple, questions about packing of nanoparticles as well as surface coverage need to be addressed. Early report of the assembly of nanoparticles into thin films by Lvov *et al* demonstrated that after the deposition of each layer, the thickness increase corresponded to the thickness of either the polyelectrolyte monolayer or the nanoparticles diameter. On the other hand, other researcher reported a thickness increase equivalent to two or three nanoparticles diameters. These discrepancies in thickness increases are probably due to different interaction with the previously adsorbed polyelectrolyte. Loops and tails from previous layer can become entangled with nanoparticles and induce the deposition of more than expected in a single monolayer. The opposite trend was observed with hydrophilic nanoparticles which resulted in the deposition of layers with less than a full densely packed monolayer. The packing of the nanoparticles into monolayers was shown to be dependant on the charge density of the nanoparticles. The particles size also played a role in the formation of densely packed layer with the highest packing obtained with smaller particles. These small nanoparticles also displayed a faster kinetic of deposition. Two deposition modes have been described by Kotov *et al.* [126] and could be summarized as normal growth mode and lateral expansion mode. The former is obtained when sequential adsorption of nanoparticles is obtained and the later correspond to an in-plane growth of isolated domains. In 2001, Caruso [132] reported the layer-by-layer assembly of metallic nanoparticles into thin films. They demonstrated the growth of the film by monitoring the

increase in absorbance as a function of the number of layers. In such methods, gold nanoparticles can be prepared using sodium citrate as a stabilizing agent and reductant result in negatively charge nanoparticles. These negative particles can be deposited into thin films using the PEM technique in sequential fashion with a cationic species such as chitosan or poly(diallyl dimethylammonium chloride). Silver nanoparticles were prepared in presence of carboxylic containing polymer and were also deposited in layered thin films.

For the formation on metallic nanoparticles thin films, three main methods have been described. In a first approach, summarized in Figure 2.15, metallic nanoparticles are prepared in solution in the presence of ionic stabilizing agent such as polyelectrolyte. The capped metallic nanoparticles can be further deposited into multilayer by successive deposition with an oppositely charged polyelectrolyte. The thickness of the film prepared using this method is mainly controlled by the number or dipping cycles. This method is probably the most widespread and published. One of the drawbacks of this method is that the nanoparticles must be stabilized by a surfactant carrying electrostatic functional groups.

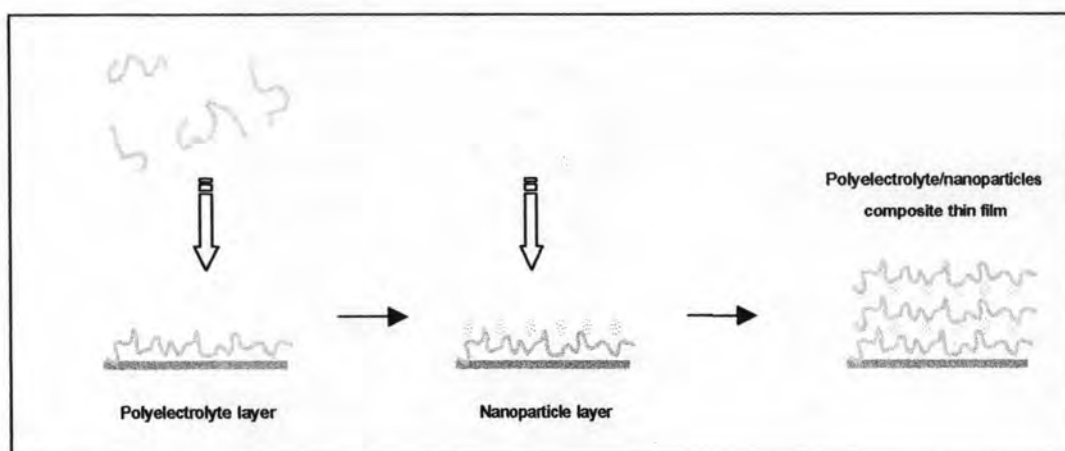


Figure 2.15: Layer by layer assembly of nanoparticles by successive coating

A second method which can be used for the preparation of metallic nanoparticles nanocomposite thin films was recently proposed by Chen and Dong [136] and is detailed in Figure 2.16. In their work the metallic ions are immobilized by

complexation with a polyelectrolyte carrying the opposite charge such as gold chloride ( $\text{AuCl}_4^-$ ) and PDADMAC. By mixing the appropriate mole ratio of PDADMAC and  $\text{AuCl}_4^-$  the PDAD retain sufficient cation groups to be deposited in multilayer fashion with PSS. The  $\text{AuCl}_4^-$  complexes display a strong yellow color which can be monitored during the deposition of the complex into the PDAD/PSS multilayer. Once the number of desired layer was deposited the gold complex were then reduced by heating at  $200^\circ\text{C}$  for 30 min leading to a color shift of the film from yellow to red which is the characteristic color of gold nanoparticles. Another similar use of in situ preparation of semi-conductor nanoparticles was given by Xiong *et al* who used Cadmium neutralized polystyrene sulfonate deposited in a layer by layer fashion with poly (vinyl pyridine). The exposure of the Cd enriched film to a stream of  $\text{H}_2\text{S}$  gas lead to the formation of CdS nanoparticles. This technique is not exactly describing the assembly of nanoparticles into thin films but the subsequent formation of nanoparticles based on the assembly of an ion rich PEM film. One of the main advantages of this technique is that it does not require the use of any surfactant since the nanoparticles are prepared in situ in the bulk of the multilayer. Another advantage with this method is that it does not require the use of sodium borohydride which is common reducing agent for the preparation of gold nanoparticles. This route provides a chemical free process which is more green and safer to be developed into industrial applications.

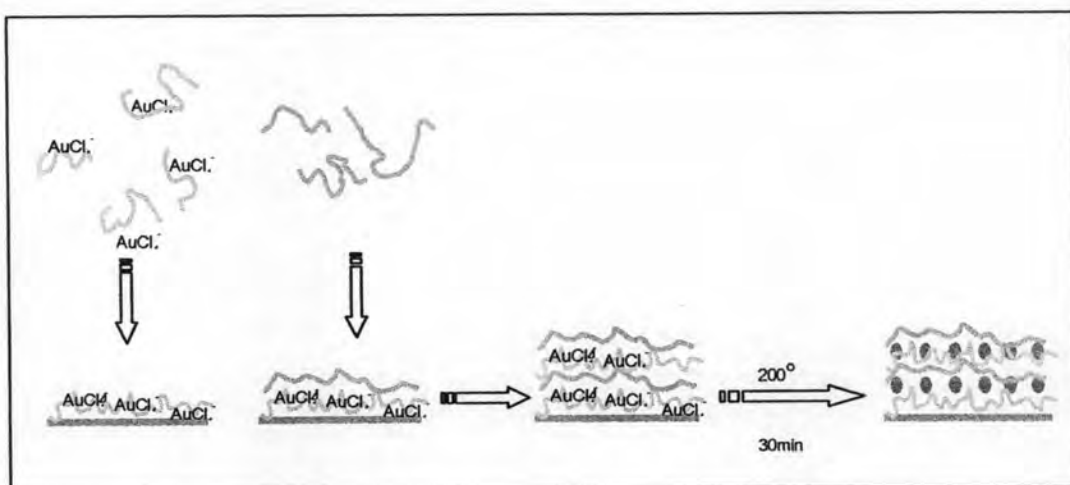


Figure 2.16: In situ preparation by co-adsorption of metallic ions

The last method reported for the preparation of metallic nanoparticles is the post-deposition in situ preparation of metallic nanoparticles shown in Figure 2.17. This technique was first proposed by Rubner et al. [114] is also referred to as electroless metal nanoparticles preparation on polyelectrolyte multilayer platform. This technique is somewhat similar to the previous method in the sense that the nanoparticles are formed after the formation of the PEM film but differ by the fact that in this method the metallic ions are not co-deposited in the multilayer. In this technique the PEM film is first deposited from carboxylic containing polyelectrolytes and poly(allylamine chloride) and then immersed in a solution containing the metallic ions. By increasing dipping time and dipping cycles they have demonstrated that ions can diffuse to some extent in the PEM film and dope the film. The entrapped metallic ions can then be reduced by various method such as hydrogen gaz, exposure to sodium borohydride solution or even heating. This method is very simple as produce film having a metallic loading of nanoparticles up to 50%. The type of metallic salt used can be varied to palladium, platinum, gold or silver. The resulting film doped with metallic nanoparticles display excellent conductivity as well as mechanical stability.

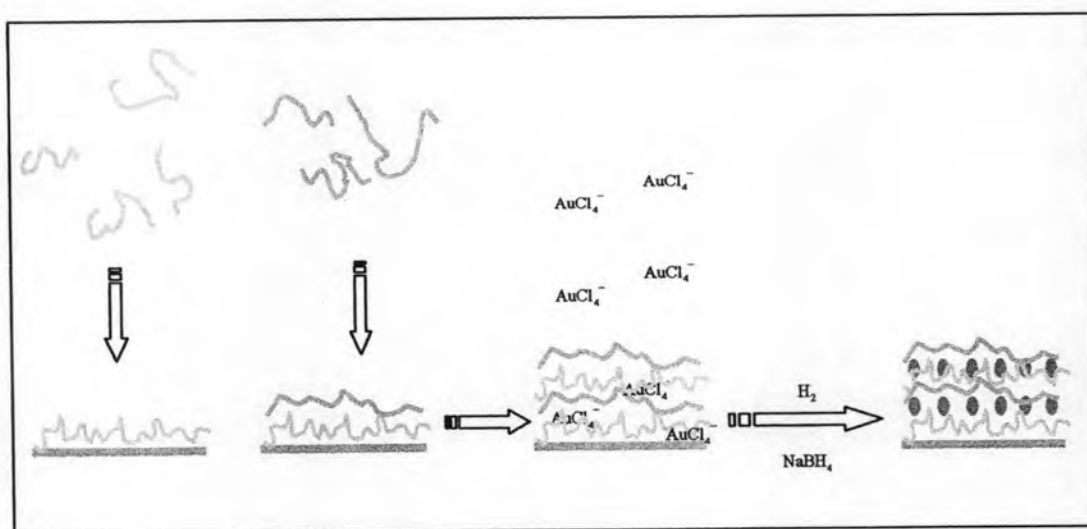


Figure 2.17: In situ preparation of nanoparticles ions doping followed by reduction

## 2.5 Characterization of polyelectrolyte multilayers

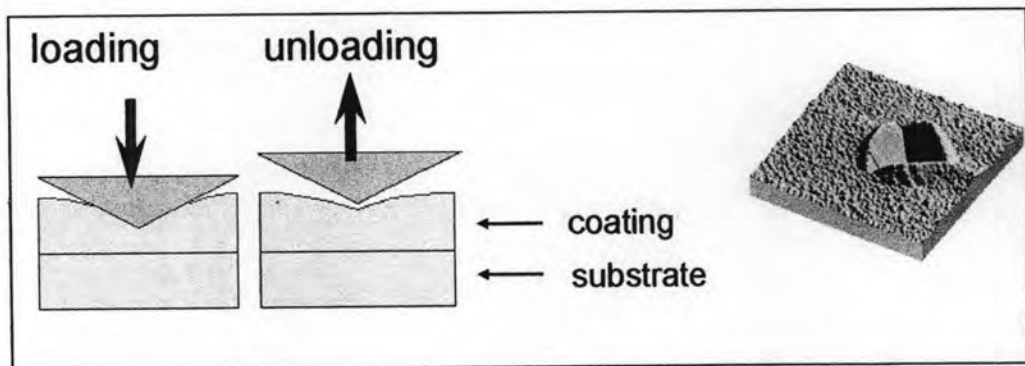
In the past 15 years, a very wide range of techniques have been used, adapted and developed for the study of the formation, stability and properties of polyelectrolyte multilayers. These techniques can be used to probe different properties of the thin films and for example, the thickness of a film can be measured by X-Ray small angle reflection, Ellipsometry, Atomic Force Microscopy. The chemical composition can be evaluated by UV-Vis spectroscopy, IR spectroscopy and X-Ray photoelectron spectroscopy. The morphology and surface properties can be evaluated by contact angle measurement, transmission electron microscopy, confocal optical microscopy, scanning electron microscopy. Lastly, the kinetic of the formation of polyelectrolyte multilayers can be evaluated by Quartz crystal microbalance, surface plasmon resonance and Attenuated total internal reflection Fourier transform infrared. To evaluate the mechanical properties of polyelectrolyte multilayers, DMA as well as nanoindentation can be used.

## 2.6 Nanoindentation

For engineers as well as Scientists, the knowledge of the hardness of a given material is of great interest. While hardness can be defined as the material's resistance to deformation, an accurate quantitative evaluation of its value is not trivial. In the past century, indentation has been widely used to this end mainly because the technique is very simple to perform, requires minimal sample preparation/mounting and can be repeated several times on the same sample. The recent development of the AFM has revolutionized the indentation technique as it now allows the applied indentation force to be controlled down to the Pico Newton with a displacement down to the nanometer. Using the AFM, virtually any solid can be indented, including bulk materials, biological entities and nanostructures. However, the strain fields under an indenter are complex and even for bulk isotropic materials, analysis of data is non-trivial. In order to be used as a nanoindenter, the AFM needs to be modified and equipped with a diamond tip mounted on a stainless steel cantilever for nanoindentation measurements. The nanoindentation is useful when the more traditional indentation technique cannot be



used for example on thin films. In 1989 Burnham and Colton [142] pioneered the use of AFM-like instruments as nanoindenter to measure nanomechanical properties of surfaces. Indentation tests, sometimes called hardness tests, are probably the most commonly applied means of testing the mechanical properties of materials. In a traditional indentation test, a hard tip whose mechanical properties are known (frequently made of a very hard material like diamond) is pressed into a sample whose properties are unknown. The load placed on the indenter tip is increased as the tip penetrates further into the specimen and the load may be held constant for a period or removed.



*Figure 2.18: Indentation process used to characterize the mechanical properties of coatings.*

The principle in nanoindentation is similar to indentation at the difference that the indenter is of a much smaller scale of few microns in size and attached onto a cantilever. The nanoindenter will only apply forces in the range of nano-newton to micro-newton. The resulting indent is also much smaller and cannot be observed with an optical microscope and require an AFM imaging system.

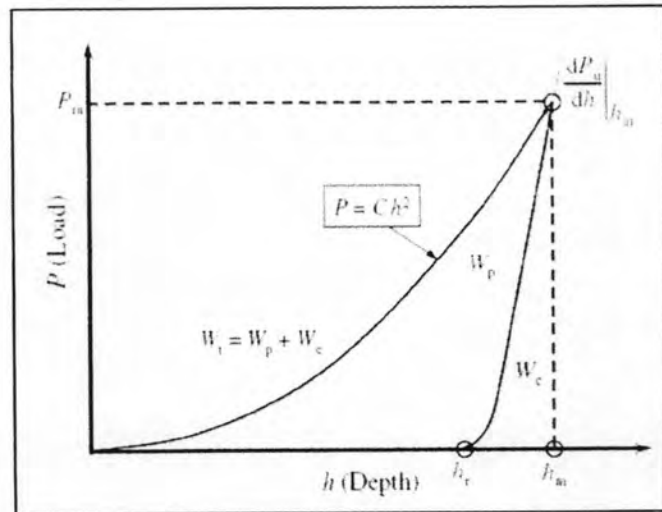


Figure 2.19: Typical depth / load curves obtained in a nanoindentation experiment.

Since its development, the AFM has proven to be a useful for studying surface interaction and elasticity my means of forces-distance curves. From the indentation depth and forces-distance curves information such as hardness and stiffness can be obtain as well as modulus. Although very powerful, the AFM present serious drawbacks which can seriously influence the accuracy of the measurement. The Stiffness of the AFM tip is provided by the fabricant but is difficult to check, the piezoelectric which drive the AFM tip motion has some hesterisis which render the depth measurements inaccurate.

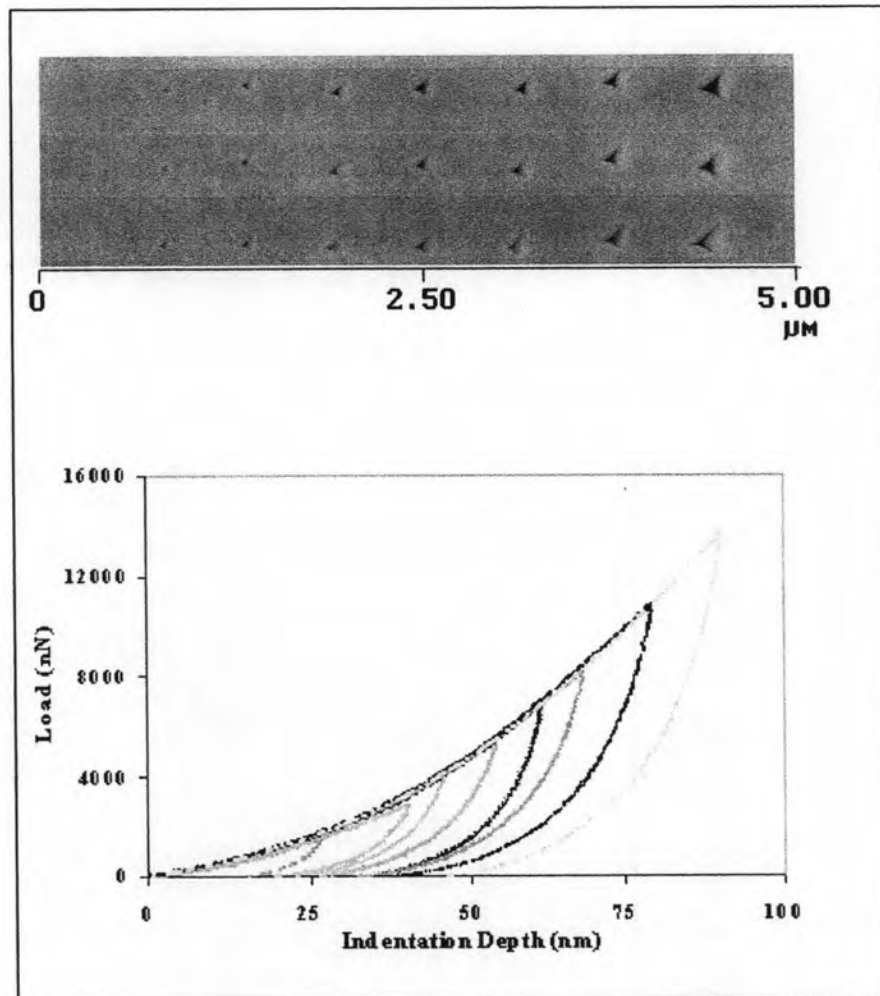


Figure 2.20: (A) AFM image of a series of indentation made using a Berkovich tip onto a sample and (B) corresponding indentation depth / load curves.

The modulus of elasticity is obtained by measuring the slope of the curve,  $dP / dh$ , upon unloading is indicative of the stiffness  $S$  of the contact. This value generally includes a contribution from both the material being tested and the response of the test device itself. The stiffness of the contact can be used to calculate the reduced modulus of elasticity  $E_r$  as

$$E_r = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A(h_c)}}$$

where  $A(h_c)$  is the area of the indentation at the contact depth  $h_c$  (the depth of the residual indentation), and  $\beta$  is a geometrical constant on the order of unity.

Concerning the hardness of the coating, two different types of hardness that can be obtained from a nanoindenter: one is as in traditional macro-indentation tests where one attains a single hardness value per experiment; the other is based on the hardness as the material is being indented resulting in hardness as a function of depth.

$$H = \frac{P_{max}}{A_r}$$