CHAPTER IV

RESULTS AND DISCUSSION

4.1 Chapter planning

In this chapter, the results from each parts of the experimental section are presented and discussed. As stated in the introduction, this chapter covers all six parts of the research work including the characterization of silver nanoparticles capped with polyelectrolytes (section 4.2), the evaluation of their sensing properties (section 4.3). The nanoparticles were then assembled in monolayers and the parameters controlling the growth of the monolayer film were studied (section 4.4). The effect of the polyelectrolyte concentration on the growth of the multilayer film as well as its effect on the mechanical properties of the film was evaluated (section 4.5). The sensing properties of the silver nanoparticle thin film toward ethanol and methanol mixed with water were evaluated (section 4.6). Finally, the surface modification of the sensing film to improve the sensitivity of the film was studied (section 4.7). These different sections of this research are summarized in Figure 4.1.

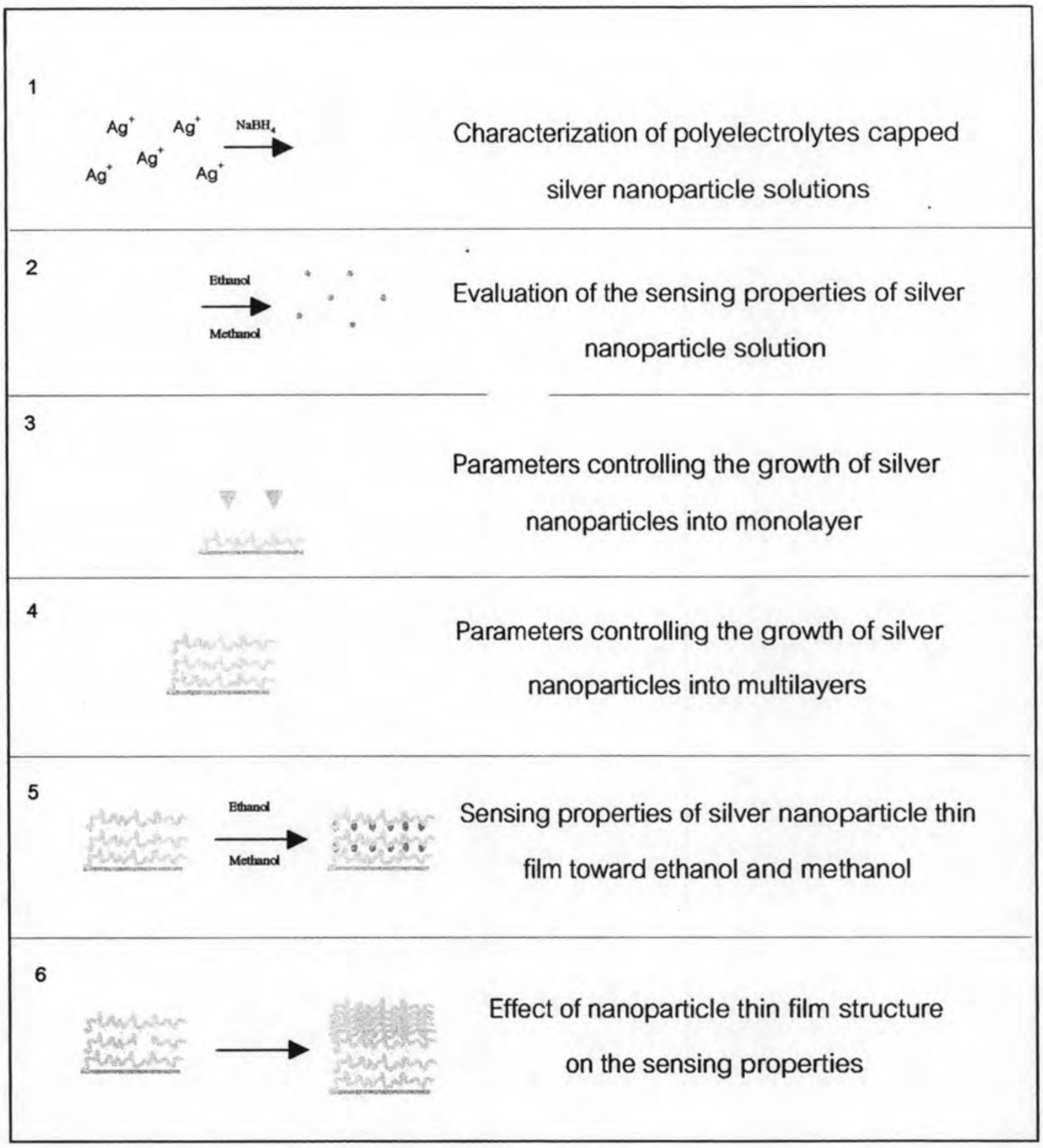


Figure 4.1: Summary of the experimental sections presented in this research.

4.2 Characterization of polyelectrolytes capped silver nanoparticle solutions

Silver nanoparticles were prepared by mixing polyelectrolytes in silver nitrate solution. The reduction of the silver ions was achieved by adding sodium borohydride. Two parameters were varied in the preparation. They were the molar ratio of polyelectrolyte with silver nitrate (10:1, 5:1, 1:1, 0.5:1 and 0.1:1) and the type of caping agent (PMA, PAA, Alginate, CoPSS and HA).

In contrast with typical methods used for the stabilization of metallic nanoparticles, silver nanoparticles were stabilized using polyelectrolytes in this research. Five types of polyelectrolytes were used namely: Sodium Alginate (alginate), Poly(styrene-co-Maleic acid, sodium salt) (CoPSS), Poly(methacrylic acid, sodium salt) (PMA), Poly(acrylic acid, sodium salt) (PAA) and Humic Acid (HA). The stabilization is needed to prevent the growth of the nanoparticles. This process occurs during the formation of the nanoparticles when a capping agent adsorbs at the nanoparticles surface. Depending on the nature of the capping agent used, the stabilization effect can be provided by two different mechanisms involving either steric hindrance or electrostatic repulsion [24]. In the present case, it was the electrostatic repulsion mechanism which was chosen for the stabilization of the silver nanoparticles. The chemical structures of five polyelectrolytes used were previously given in Chapter 3 and it should be noted that they all presented anionic character. More specifically, they all beard some carboxylate functional groups along their carbon backbone. Carboxylic functional groups are known to interact and adsorb onto metallic surfaces and are expected to adsorb onto the silver nanoparticle [75]. The nanoparticles formed in solution through nucleation growth displayed a characteristic of vivid yellow color which is due to the surface plasmon absorbance phenomenon (LSPR). Theoretical insights on this phenomenon were given in Chapter 2. Because nanoparticle solutions present intense yellow color, UV-Vis spectroscopy can be used to monitor and quantify the presence of nanoparticles in solution or in films. In fact, silver nanoparticles could be compared with chromophore but differ in their method of interaction with the light and absorption of the light. Because the position of the LSPR band is located around 400 nm, UV-Vis technique has proven to be a very simple and versatile technique for the study of silver nanoparticles. Most publications published in the field presented UV-Vis spectra as the evidences of the presence or the formation of silver nanoparticles.

4.2.1 Study of the effect of the [polyelectrolyte]:[silver nitrate] ratio

UV-Vis spectra of silver nanoparticles using different polyelectrolytes with the concentrations of 0.1, 0.5, 1, 5 and 10 mM are shown in Figure 4.2. The concentration of silver nitrate was kept fixed at 1 mM and the concentration of sodium borohydride ($NaBH_4$) at 10 mM in all experiments. $NaBH_4$ is often used as a reducing agent in the preparation of silver nanoparticles was used in excess in order to ensure full reduction of Ag^+ ions. When $NaBH_4$ is hydrolyzed by water, hydrated electrons and H_2 gas are produced inducing the reduction of silver ions. Because the mixing of various chemicals is not immediate, $NaBH_4$ is prepared ahead of time which raise some concerns about the kinetic of hydrolysis and how long could the solution be used for the reduction experiment. The activity of $NaBH_4$ solutions for more than 3 hours was demonstrated by reducing silver salts with aliquot of $NaBH_4$ solutions taken at 30 minutes of intervals and then measuring UV-Vis absorbance spectra of these solutions. The results are not shown here but the solutions prepared with same $NaBH_4$ stock solution had the same UV-Vis spectra without significant differences seen between each solution. This experiment confirmed that $NaBH_4$ can be used for more than 3 hours without any loss of efficiency in the reduction of silver salts. The solution containing silver nanoparticles were then placed in quartz cuvette and their optical properties evaluated with a UV-Vis spectrophotometer in the range of 190-700 nm. This range was chosen because it covers the nanoparticles' LSPR located around 400 nm and the absorbance of the polyelectrolytes used which is located around 200 nm. Polyelectrolytes which do not carry any conjugation of chromophore absorb usually UV light through excitation of chemical bonds such as carbonyl. The valence electrons are excited from σ or σ^* to π. These electronic transitions require high energy which is found in UV light of wavelength around 200 nm. It can be seen that all the prepared solutions had yellow color characteristic. Also, the maximum peak position of each solution was found to be located around 400 nm which confirm the successful preparation of silver nanoparticles for each polyelectrolyte concentration used. Polycationic polyelectrolytes were unsuccessful to stabilize the nanoparticles probably due to repulsive interaction with cationic Ag^+. Alginate appears to be a good capping agent for the preparation of silver nanoparticles. 0.1:1 molar ratio seems to be sufficient to stabilize the nanoparticles and prevent Ostwall ripening. It is probably the rich content in carboxylic and hydroxyl groups which are responsible for the stabilizing effect.

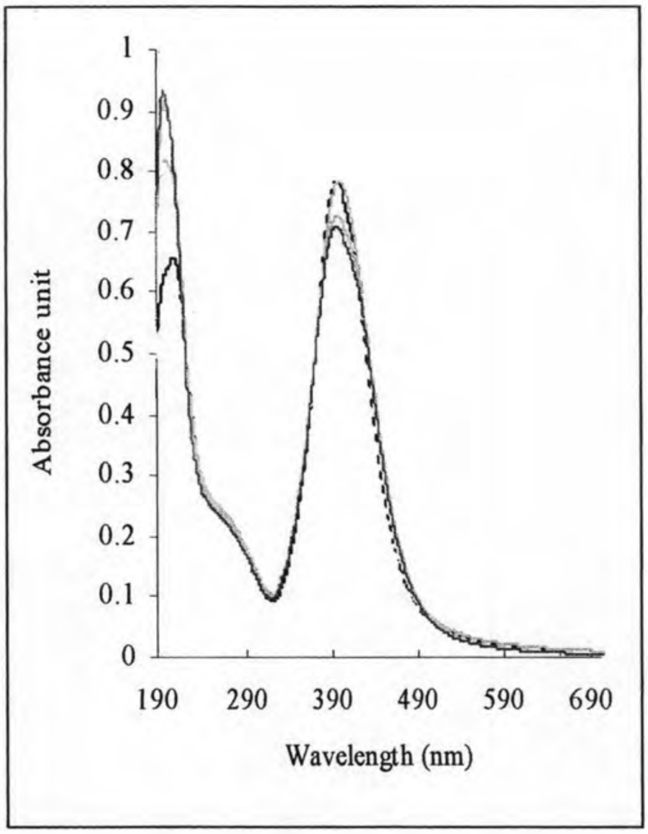


Figure 4.2: UV-Vis spectra of silver nanoparticles solutions capped with 10 mM (purple), 5 mM (light blue), 1 mM (pink), 0.5 mM (yellow) and 0.1 mM (blue).

4.2.2 Effect of the type of capping agents

Although all the selected polyelectrolyte solutions could be used, they had interesting and significant differences. In every case of nanoparticle preparation, when the concentration of polyelectrolyte was increased, the peak width at half height decreased. The height corresponds to the maximum absorbance at λ_{max} and the width is the spectrum width in nanometer at half λ_{max} absorbance. This width factor was reported by Mafune *et al.* [140] to be representative of the size distribution of silver nanoparticles dispersed in solution when the nanoparticles size exceeded 10 nm. Using this number, it is expected that lower width in nm corresponds to narrow dispersion of particles in size.

From Figure 4.3, it can be seen that alginate and PMA provide more uniform silver nanoparticle solutions within a wide range of concentrations while CoPSS and PAA lead to more disperse solutions. The good stability of alginate and PMA capped solutions can be explained by the rich content of these polyelectrolytes in carboxylic functional groups which are known to bind and therefore stabilize the silver nanoparticles.

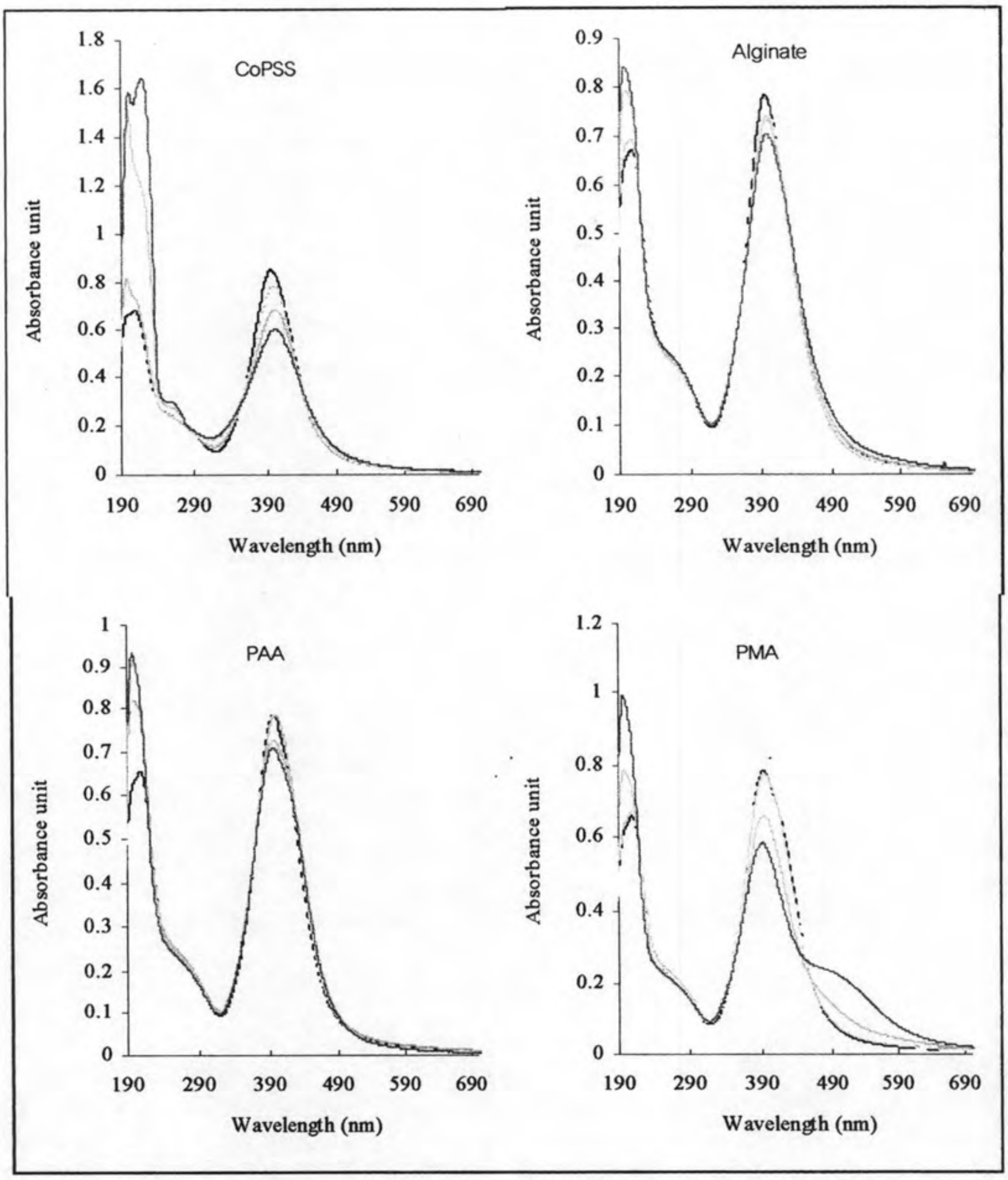


Figure 4.3: UV-Vis spectra of silver nanoparticle solutions using different types and concentration of capping agents [10 mM (blue), 5 mM (pink), 1mM (Yellow), 0.5 mM (turquoise), 0.1 mM (purple)].

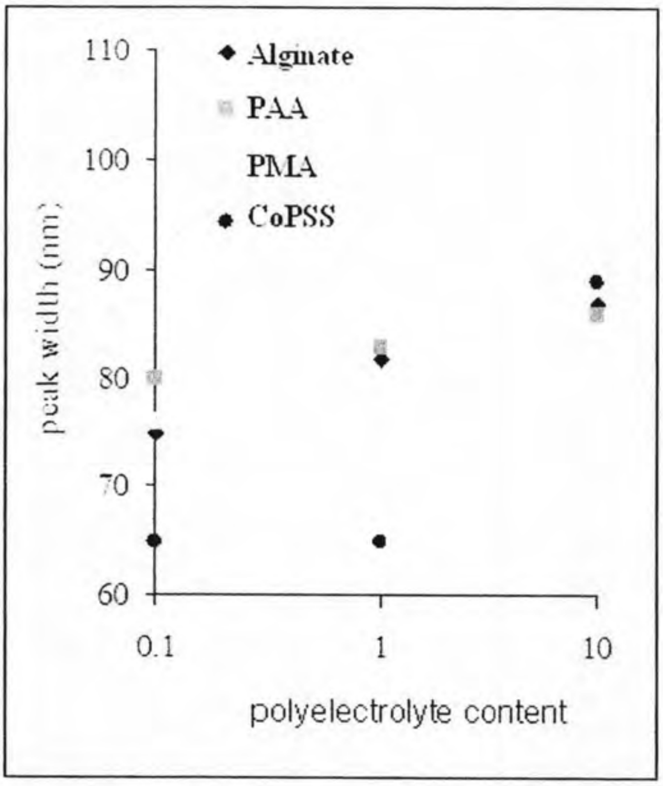


Figure 4.4: Plot of the peak width at half absorbance maximum for PMA, PAA, CoPSS and alginate as a function of the polyelectrolyte content used in the preparation of the nanoparticles.

From Figure 4.4, it can also be seen that the peak around 200 nm increases with increasing polyelectrolyte content which is expected since the absorbance is proportional to concentration however the relationship appears to be non-linear. Absorbance at 200 nm of the prepared solutions as a function of polyelectrolyte concentration is plotted in Figure 4.5. For the solution in which CoPSS is used, the absorbance increased linearly as polyelectrolyte concentration increased suggesting a poor interaction between the polyelectrolyte and the surface of the nanoparticles. This confirms the broad size of UV-Vis plasmon band in the case of CoPSS when compared with other polyelectrolytes. In the case of PMA, alginate and PAA, the absorbances at 200 nm increased slowly for the solutions having concentrations between 0.1 and 1 mM. It can be speculated that low polyelectrolyte concentration is due to the capping of silver nanoparticles which consumed the polyelectrolytes in solution. As the concentration of silver nitrate was kept constant, the total number of nanoparticles might vary due to different particle size but not in the range of polyelectrolyte concentrations which were increased 3 orders of magnitude from 0.1 to 10 mM. In the mean time the absorbance peak of silver nanoparticles capped with alginate is seen to increase slightly suggesting that the polyelectrolytes were consumed by adsorption onto the surface of the nanoparticles. These results should be confirmed by measuring the amount of polyelectrolytes left in solution. It will be shown later that these excess polyelectrolytes induced a competitive adsorption which prevented nanoparticle deposition from high polyelectrolyte content solutions.

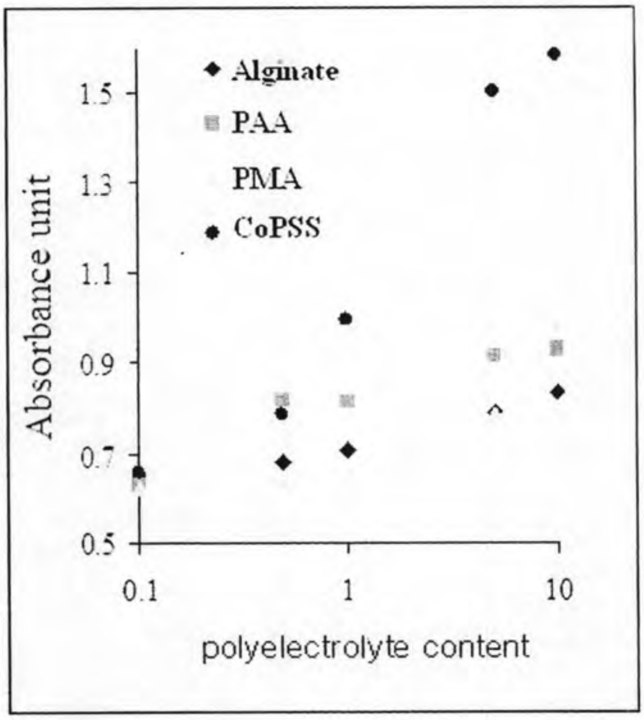


Figure 4.5: Plot of the absorbance at maximum wavelength of nanoparticles solution prepared with different capping agent as a function of their concentration.

4.2.3 Characteristics of humic acid capped silver nanoparticles

The results of HA capped silver nanoparticles are presented separately from the other polyelectrolytes because HA, although being an electrolyte is not a polyelectrolyte. HA are macromolecules found in organic substance in the soil of forests with a molecular weight ranging from 50 KDalton to 300 KDalton. HA structure is mainly aromatic rings which give them a hydrophobic character. HA also includes hydrophilic hydroxyl and carboxylic groups as well as sulfur thiols which can bind strongly at the surface of metals such as gold and silver. HA was used in this research as a capping agent due to its chelating potential towards metals and metallic ions. Although the composition of HA has not been exactly established and is likely to depend on the source of HA, strong interaction between HA and silver ions have been explained by the high HA content in nitrogen and oxygen which both are electron donors [32-34]. Another factor favoring the immobilization of silver ion in HA macromolecules is the presence of up to 3 atomic % of sulfur. This element is known to interact strongly with metallic ions through the formation of a thiol-metal bond. For all these reasons, HA can be easilly used as a capping agent for the preparation of silver nanoparticles. One of the difficulties when using HA was that the solution had a very deep brown/black color which makes the monitoring of silver nanoparticles formation difficult. Nevertheless, diluted solutions of HA having a concentration lower than 0.01% w/w appeared clear enough that the formation of silver nanoparticles could be confirmed by UV-Vis spectroscopy after background subtraction. In Figure 4.6, the corrected spectra can be seen but due to extensive background subtraction, spectra D and E are to be analyzed with caution. Similarly to the peak width observed when using polyelectrolytes, HA capped nanoparticle solutions present narrower spectrum at lower HA content. It is possible that high HA content due to its hydrophobic character induced particle aggregation causing broader spectrum. Although narrower size distribution can be assumed from narrow spectra, these solutions also present the poorest stability when compare with solutions of nanoparticles prepared using higher HA concentration.

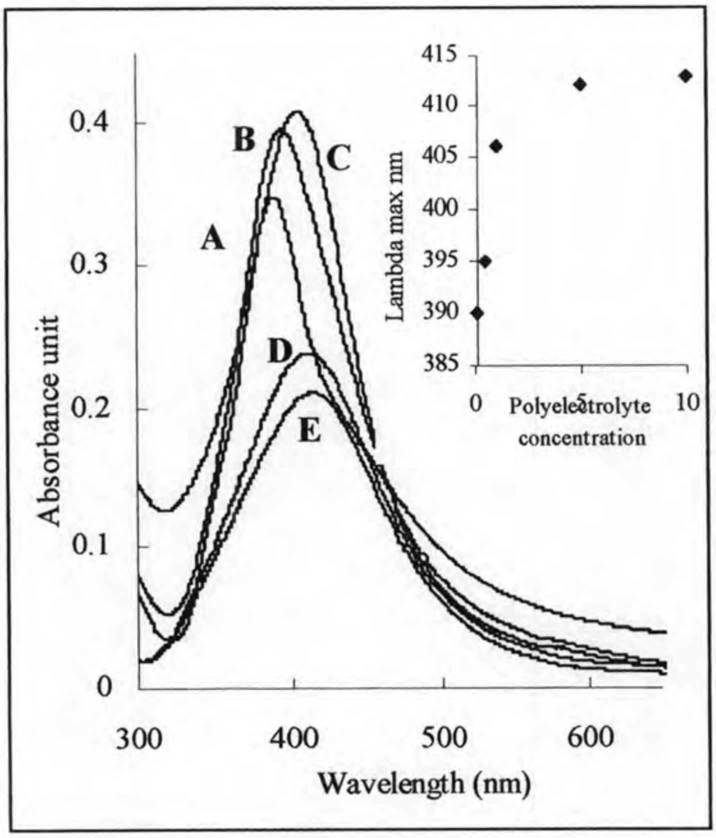


Figure 4.6: Extinction spectra of silver nanoparticle solutions prepared with different HA concentrations [(A: 0.01 mg/ml), (B: 0.05 mg/ml), (C: 0.1 mg/ml), (D: 0.5 mg/ml) and (E: 1 mg/ml)].

It can be observed from Figure 4.6 that the spectra with the most red shifted absorbance maxima (spectrum E) corresponds to the highest HA content while the absorbance spectrum A correspond to the least amount of HA substance added. This shift of the plasmon band to higher wavelength with higher HA content (shown in the cartouche of Figure 4.6) can be explained by a more dense coating of hydrophobic HA substance, which affects the value of the dielectric constant of the medium surrounding the nanoparticles. Such observations were previously reported as well as predicted by LSPR modelisation. In their work Xu and Kall [140] reported the dependence between the thickness of a polymeric coating of PMMA onto silver nanoparticles and the LSPR shift. In their work, various PMMA coatings of thickness ranging from 0 to 15 nm induced a shift in the position of the plasmon band absorbance maximum of up to 20 nm. The thicker the coating the more red shifted was the spectra.

In their work, they also showed that smaller particles were more sensitive to coating thickness and had a greater shift than bigger particles for a given coating thickness. Similar phenomenon is likely to be the cause of the observed plasmon shift as a function of the HA content.

4.2.4 Morphology of humic acid capped silver nanoparticles

The size of silver nanoparticles was confirmed by TEM and its image is shown in Figure 4.7 which revealed an average particle size distribution of 5 nm (Figure 4.8). THe specific metal-ligand bonds between silver nanoparticles and HA stabilized the sols for several months. Thiols based capping agents are commonly used in the preparation of silver nanoparticles. The shape of nanoparticles appeared to be spherical and no sign of aggregation is visible which confirm the good capping effect provided by HA.

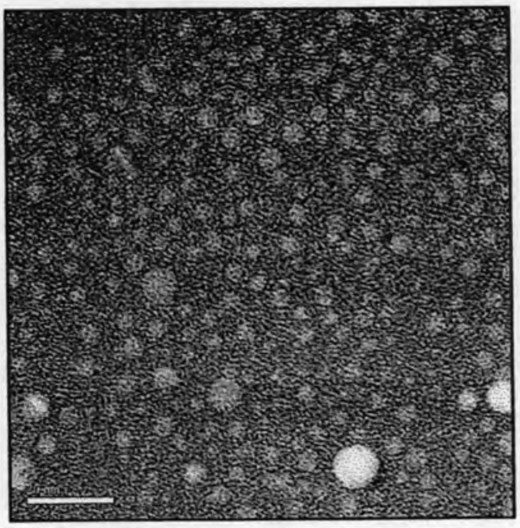


Figure 4.7: Transmission electron microscopic image of silver nanoparticles from 0.1mg/ml silver nitrate and 0.01mg/ml of HA. (scale bar = 20 nm)

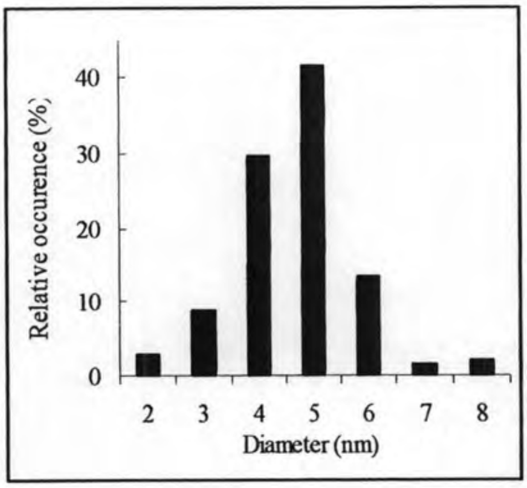


Figure 4.8: Relative size distribution of HA capped silver nanoparticles prepared from 1mg/ml silver nitrate and 0.01mg/ml of HA.

4.3 Sensing properties of silver nanoparticle solutions

Since this work concern the preparation of silver nanoparticles for sensing applications, changes in optical properties of silver nanoparticles were evaluated by mixing the nanoparticle solution with various organic compounds. The selected organic compounds were methanol, ethanol, propanol and acetone. The nanoparticles were the ones described in the previous section which contained the capping agents as Alginate, PMA, PAA, CoPSS or HA. The polyelectrolyte concentrations used in the preparation were varied from 0.1 mM to 10 mM and the silver nitrate concentration was fixed to 1 mM.

4.3.1 Effect of the capping ratio on the sensing properties of alginate capped nanoparticles

Because nanoparticles were dispersed in water, the exposure to the organic compound could not be of 100% and instead it was 90% of organic compound with 10% of water. Figure 4.9 exhibits that the spectral shift obtained when the nanoparticles capped with various contents of alginate were exposed to a 90% ethanol solution in water. It can be seen that the nanoparticles capped with 10, 5, 1 or 0.5 mM alginate do not display any color shift when exposed to ethanol. Only 0.1 mM capped nanoparticles displays a shift in absorbance upon mixing with ethanol. It can be seen that the characteristic LSPR peak at 400 nm decreases and a new peak at 510 nm appears. This optical response is very similar to the response obtained when mixing herbicide with HA capped nanoparticles. The justification of such optical shift is again probably due to the change in dielectric constant of the nanoparticles' surrounding. It is interesting to note that only 0.1 mM-capped nanoparticles solution allows this optical shift. The thicker coating of polyelectrolytes was expected to prevent the interaction between the nanoparticles surface and the organic compound. The highly electrostatic charges of the polyelectrolytes repelled the solvent which then could not change the dielectric constant of nanoparticles surrounding.

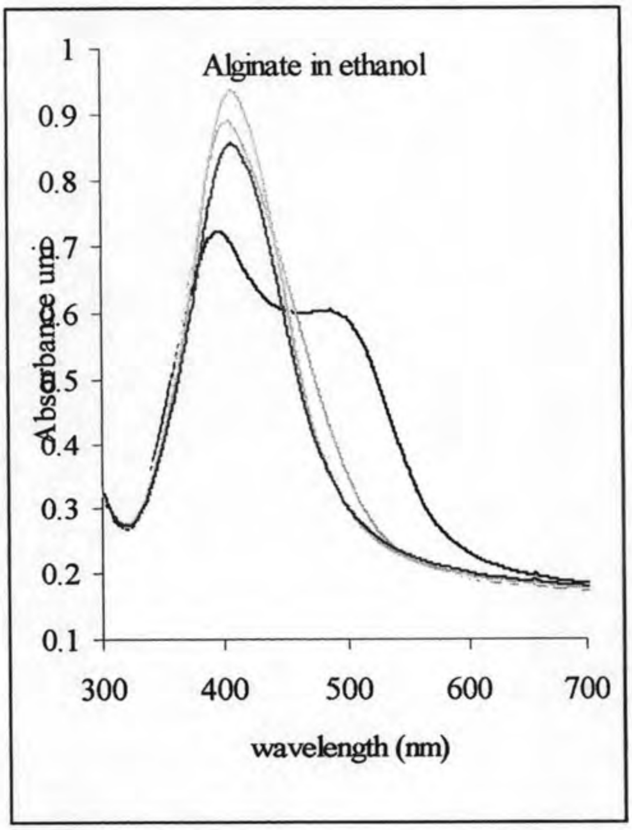


Figure 4.9: UV-Vis spectra of silver nanoparticle solutions prepared from different alginate concentrations [10 mM, (light blue), 5 mM (yellow), 1 mM (pink), 0.5 mM (purple) and 0.1 mM (blue)] and exposed to 100% ethanol solutions.

4.3.2 Effect of the type of capping agent

In Figure 4.10, the summary spectra of all 4 types of polyelectrolytes (Alginate, PMA, PAA and CoPSS) are shown when exposed to 10% of nanoparticles in water solution and 90% of organic compound. The polyelectrolyte concentration used in the nanoparticles preparation was 0.1 mM for all solutions. The spectra all display similar trend which is a red shift when the nanoparticles are exposed to organic compound of decreasing dielectric constant. Since it has been shown in the previous paragraph that only 0.1:1 polyelectrolyte to silver nitrate capping ratio led to a color change when exposed to less polar solvent, all silver nanoparticles used in this experiment were prepared from 0.1:1 ratio. The argument of the polyelectrolytes coating can also be used to justify the fact that the differences in response can be observed. Nanoparticles capped with CoPSS, which has the highest hydrophilic character among all capping agent, display the least changes when exposed to organic compound. On the other hand, nanoparticles capped with alginate had the highest response to organic compound and should be a good candidate for the formation of nanocomposite thin films. It is clear that the type of capping agent can be used to tune the optical response of the nanoparticles to organic compound of various polarities.

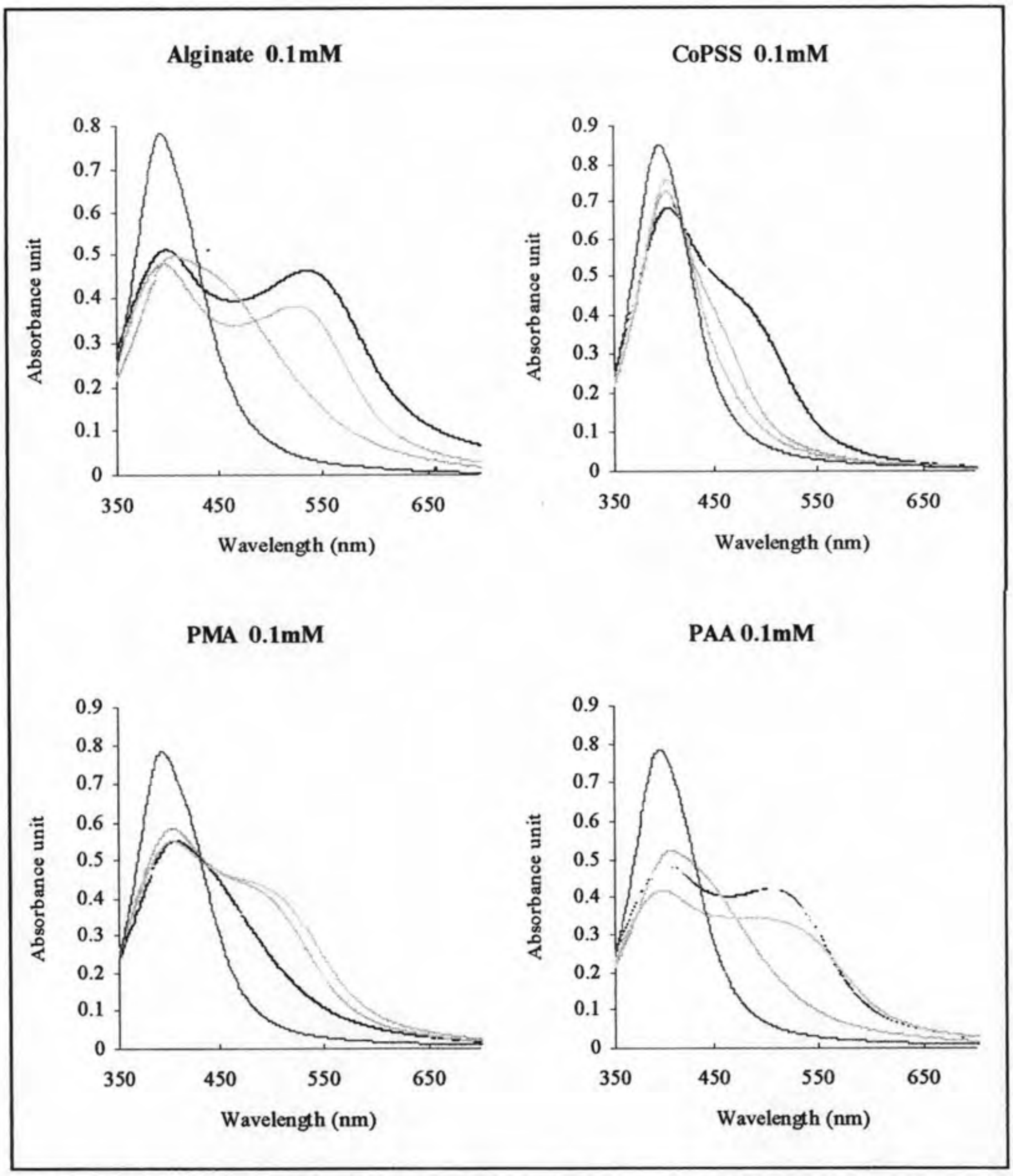


Figure 4.10: UV-Vis spectra of silver nanoparticles capped with various polyelectrolytes when exposed to different organic compounds [Water (brown); methanol (blue); ethanol (yellow); propanol (pink); acetone (light blue)].

4.3.3 Detection of herbicides by Humic acid capped silver nanoparticles

The choice of HA for the capping of silver nanoparticles was motivated by the chemistry of this substance which posses both hydrophobic (phenyl) and hydrophilic (amino, carboxylic and thiols) functional groups. These hydrophobic groups are necessary for the design of sensing system which needs to target hydrophobic herbicide molecules while hydrophilic chelating part binds to silver nanoparticles. Due to the natural dark brown color of HA solutions, silver nanoparticles prepared from higher HA content could not be used in sensing properties as the color of the solution would interfere with the optical sensing properties of the nanoparticles. Silver nanoparticles prepared from 0.001 % weight of HA were selected to be used as the sensor since they presented the best response to organic compound.

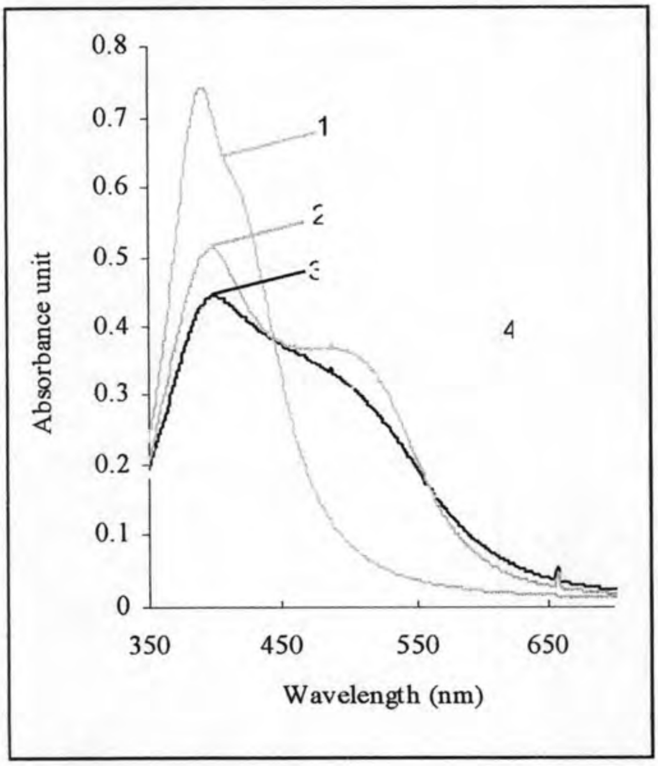


Figure 4.11 UV-Vis spectra of silver nanoparticles capped with HA when exposed to different organic compounds (1 methanol; 2 ethanol; 3 propanol; 4 acetone).

Shown in Figure 4.11 is the optical response of HA capped nanoparticles when exposed to different organic compounds. HA when compared with other capping agents provide the highest red-shifted spectra upon mixing with organic compounds. This is due to the very hydrophobic character of HA substance. The presence of benzene rings allow a strong binding with organic compounds while the carboxylic groups provide the stability in water. For these reasons HA capped nanoparticles were further tested for their applications to the design of herbicide optical sensors.

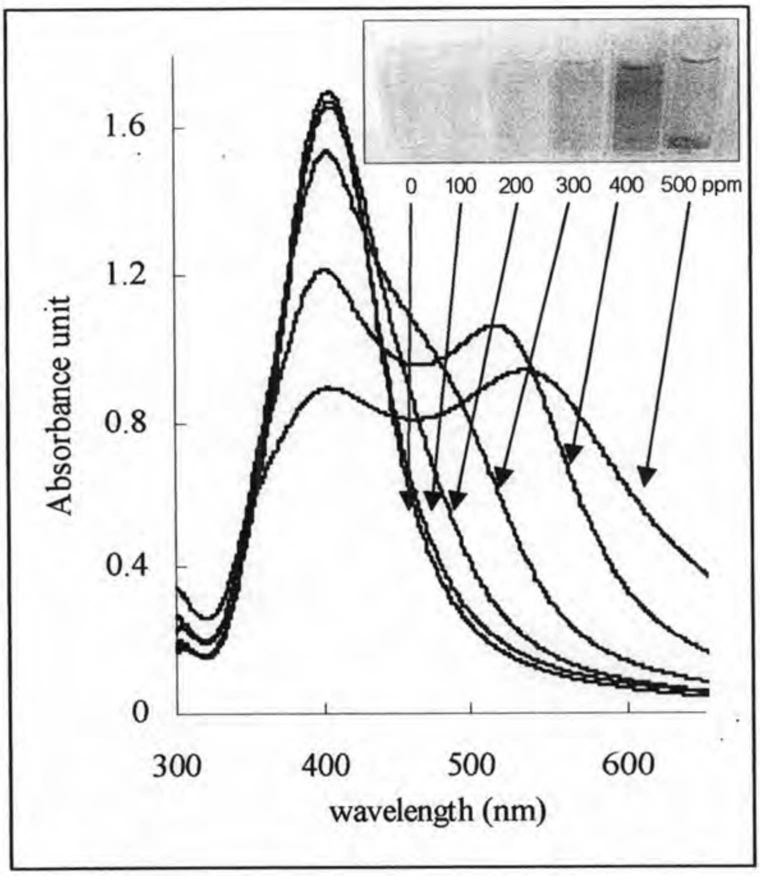


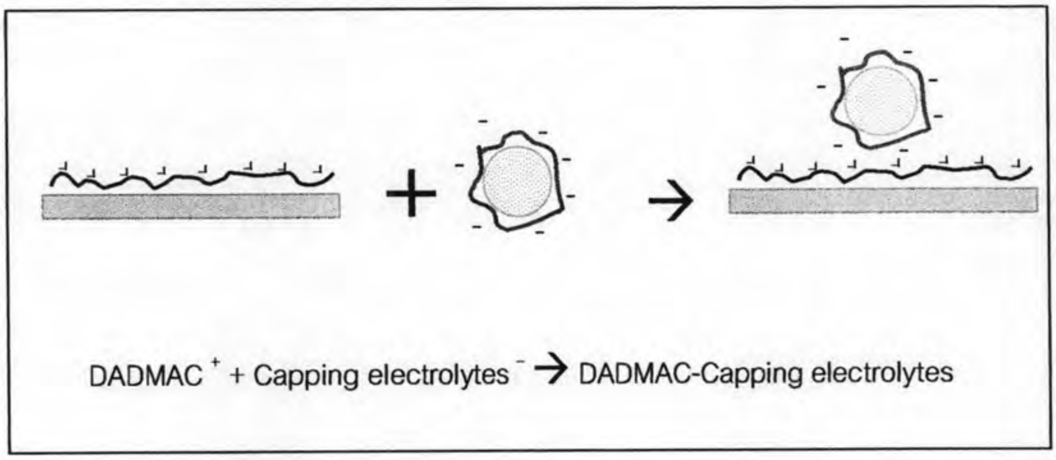
Figure 4.12: Extinction spectra of the nanoparticles solution exposed to herbicide concentrations of 0, 100, 200, 300, 400, 500 ppm.

Shown in Figure 4.12 is the change in absorbance of silver nanoparticle solutions as a function of herbicide concentration. The picture in cartouche displays the corresponding color change with increasing herbicide concentration from left to right. It can be seen that as the concentration in pesticide increases, the peak located at 400 nm decreases and a new peak appears at 530 nm. This is probably due to a decrease in particle distance with higher herbicide concentration probably caused by the aggregation of nanoparticles as it was reported with gold nanoparticles. The switch is known to occur when the distance between particles decreases to a value smaller than three particle diameter. The color of the solution varies from yellow in the initial state to orange red and purple when the concentration of the pesticide increases from 0 to 500 ppm (cartouche in Figure 4.12).

4.4 Parameters controlling the growth of silver nanoparticles monolayered films

As mentioned earlier in this chapter, the main point in using polyelectrolytes as the capping agents for the preparation of silver nanoparticles is that they can be later assembled into monolayer and later multilayers onto any substrate. The substrates used in this study were either a glass slide or a quartz slide as they allow facile monitoring of the nanoparticles adsorption using a UV-Vis spectrophotometer. The self-assembly of nanoparticles has been studied for some systems but full study of the adsorption behavior depending on the preparation condition has not yet been reported. The objective of this part is to study the effect of various parameters on the adsorption of silver nanoparticles into a monolayer thin film. These parameters include the type of polyelectrolytes, the concentration of polyelectrolytes, the ionic strength of the solution and the dilution factor. Finally, the true assembly of silver nanoparticles into monolayers was confirmed by measuring the thickness of the monolayer with AFM.

This study also concentrated on the kinetic of adsorption by measuring the changes in UV-Vis absorbance of the nanoparticle film as a function of the dipping time. The complexation process is summarized hereafter in Figure 4.13.



DADMAC$^+$ + Capping electrolytes$^-$ → DADMAC-Capping electrolytes

Figure 4.13: Drawing of the adhesion of capped silver nanoparticles onto modified glass slide with polycationic PDADMAC.

It should be mentioned that because quartz and glass slides tend to have a negative charge due to the deprotonation of silanol functional groups. Si-OH groups on the glass surface present a deprotonated form Si-O$^-$ under mild alkaline conditions. The overall negative charge would repel the negatively charged nanoparticles and therefore, prevent nanoparticle adsorption and block the deposition process. To allow the deposition of nanoparticles, the glass slide were coated with polycationic PDADMAC by dipping the substrate for 30 min in a 10 mM polyelectrolyte solution followed by a rinsing step. The irreversible adsorption of PDADMAC onto the quartz or glass substrates resulted in the reversal of the substrate charge from negative to positive and therefore, allowed the adsorption of silver nanoparticles to occur. This monolayer acts as a primer for the subsequent nanoparticle coating [78].

4.4.1 Kinetic of adsorption

In Figure 4.14, the adsorption kinetic of silver nanoparticles capped by CoPSS 0.1-1 mM as a function of time was monitored by plotting the changes in absorbance at the λ_{max} of the nanoparticles. It can be seen that at early time, from 0 to 200 seconds the absorbance of the nanoparticle film increased sharply which suggest the quick adsorption of the nanoparticles onto the glass slide. The adsorption process is mainly controlled by two independent steps which are the diffusion of metallic nanoparticles from the solution to the substrate surface and the complex formation between polycationic PDADMAC and negatively charged silver nanoparticles. While these two processes occurred simultaneously the complexation process was much faster and it is expected that the diffusion was the limiting process in this system. While it is difficult to know exactly what factor controls the final adsorption of the silver nanoparticles, several factors can have been suggested. Selective experiments allowed the separation of various factors and can be identified as follows: the type of polyelectrolytes capping, the ionic strength of the solution, the concentration of nanoparticles and the concentration of polyelectrolytes used nanoparticle preparation. These four main factors will be discussed in the following sections.

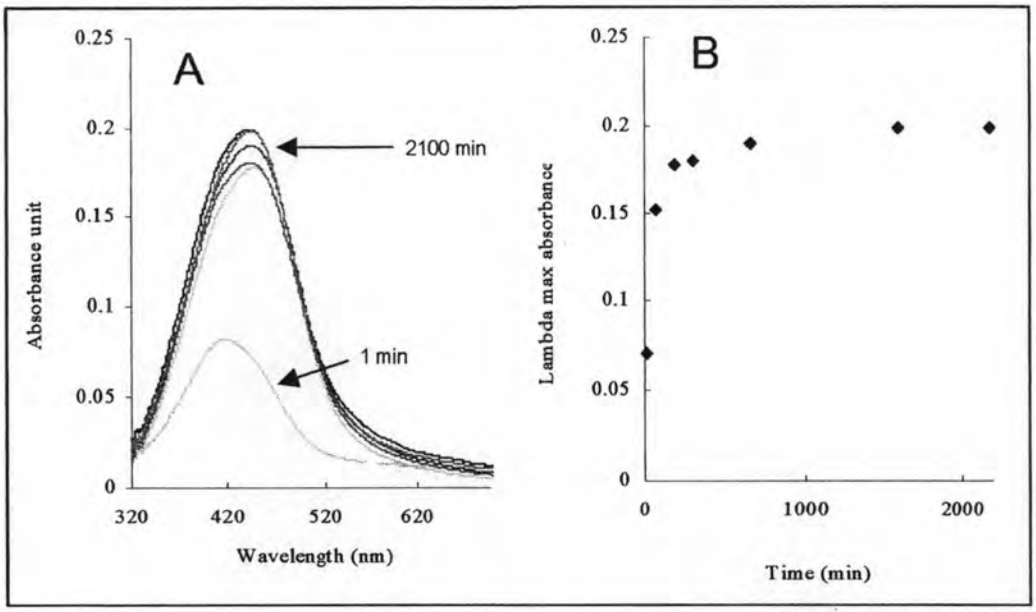


Figure 4.14: (A) UV-Vis spectra of a monolayer of silver nanoparticles as a function of time; (B) plot of the changes in absorbance at λ_{max} of the same monolayer of silver nanoparticles as a function of time.

In Figure 4.15 the changes in UV-Vis absorbance of the silver nanoparticles film as a function of time is shown. The 5 different curves represent the adsorption of nanoparticles capped with alginate, PMA, PAA, CoPSS or HA. It is interesting to observe that each polyelectrolyte capping led to a different loading of nanoparticles onto the substrate. While HA capping provided the highest surface coverage, CoPSS capping had the lowest one. An electrostatic argument can be used to explain such differences. HA is probably the most hydrophobic polyelectrolyte due to its chemical structure. HA contains numbers of aromatic rings and has a relatively low linear charge density when compared with other polyelectrolytes.

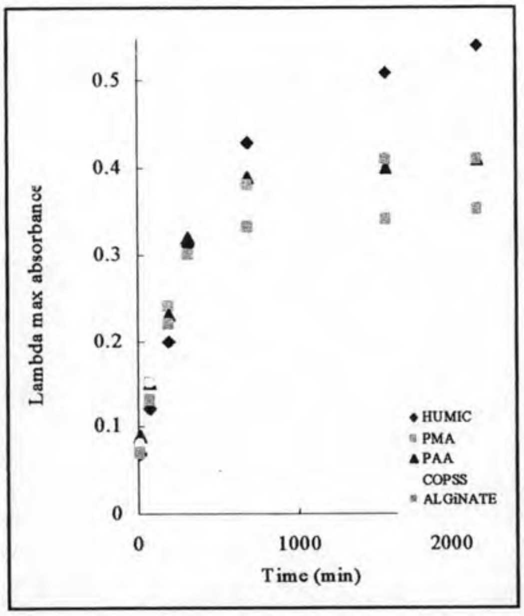


Figure 4.15: Plot of the changes in absorbance at λ_{max} of the monolayer films of silver nanoparticles prepared with different capping agents.

Previous work from Kotov [126] demonstrated that more hydrophobic nanoparticles tended to adsorb in a more packed and denser fashion. This is probably the results of low electrostatic charge and low electrostatic repulsion between particles. This lower repulsion between the particles allow for a higer packing of the particles as seen in Figure 4.15. On the other hand more hydrophilic carboxylic as well as sulfonic groups of CoPSS posses the lowest adsorption of the nanoparticles into monolayer. Yet the only hydrophilic/hydrophobic nature of the polyelectrolytes used in the preparation of the nanoparticles cannot be the only parameter affecting the adsorption behavior. Based on charge density and functional group type, PAA should be the most hydrophilic polyelectrolyte and should therefore have the lowest adsorption. Another parameter must involve in order to explain why CoPSS has a lower adsorption than PAA. This parameter could be that CoPSS, due to its low carboxylic content, might be a poor stabilizing agent in the nanoparticles preparation. In fact, PSS alone when used as a capping agent, failed to protect the particles from Ostwald ripening and upon adjunction of $NaBH_4$, the silver precipitated quickly into large particles. This suggests that sulfonic groups are poor stabilizing agent for silver. Based on these observations, it seems possible that un-reacted CoPSS polyelectrolytes would be present in the solution and induced a competitive adsorption mechanism during the monolayer formation.

4.4.2 Effect of dilution on the adsorption of 0.1 mM alginate capped silver nanoparticles

Two of the main factors controlling the adsorption rate of charged species onto an oppositely charged interface are the ionic strength of the solution and the specie concentration. The ionic strength of the solution is controlled by the concentration in electrolytes present in solution and can be adjusted by adding sodium chloride (NaCl). The effects of dilution factor of the nanoparticles solution on the kinetic of adsorption were investigated. The adsorption rates of the original undiluted solutions were compared with those of diluted alginate capped silver nanoparticle solutions as shown in Figure 4.16. The plot shows that the kinetic of adsorption from the undiluted solution is very fast and completed after only few minutes. The results show also that when the dilution increases the kinetic decreases dramatically and present a slower increase in absorbance suggesting a slower rate of adsorption of the nanoparticles onto the substrate. The interactions with surfaces are mainly noncovalent, such as H-bonding, electrostatic, and Van der Waals. Several adsorption models were used to quantify and predict adsorption rates on surfaces for example by Langmuir in 1916 which led to a simple and important theoretical derivation of an adsorption isotherm. The rate of attachment to the surface is proportional to the concentrations, and the area available for adsorption which confirms the observed slower adsorption rate for lower nanoparticles concentration.

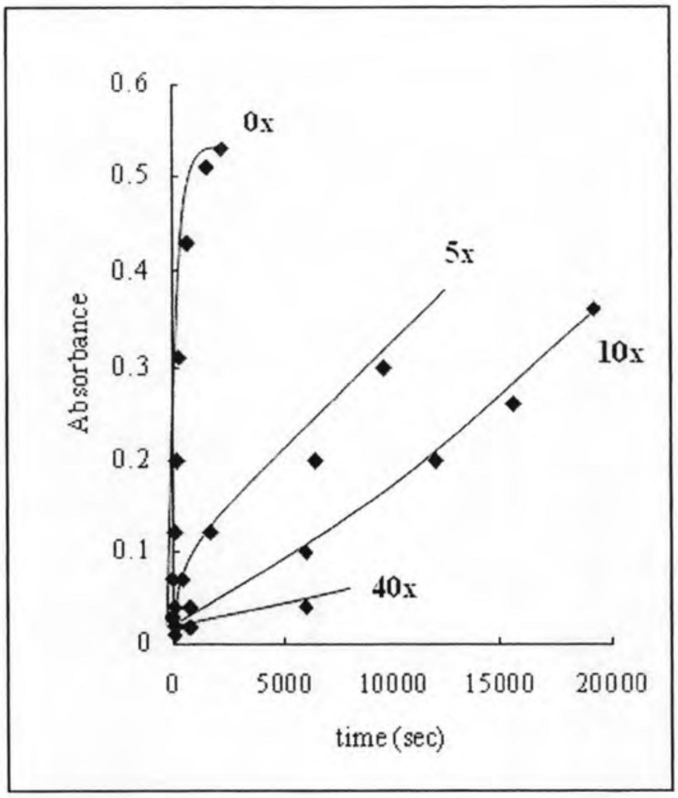


Figure 4.16: Absorbance of alginate capped silver nanoparticle thin films prepared from different dilutions conditions.

4.4.3 Effect of the ionic strength of the solution on the adsorption of silver nanoparticles

When adding NaCl in the solution, two major effects including the kinetic of adsorption and the saturation level of nanoparticles onto the film were observed. The ionic strength of the solution influenced the adsorption kinetic by modifying the distance at which electrostatic interaction can be felt by two oppositely charged particles. This distance is named the bjerum length and is the distance at which the electrostatic potential felt by a charged particle is equal to the thermal energy kT [85,86]. Seen in Figure 4.17, are the changes in absorbance of the monolayer silver nanoparticle films when NaCl concentrations were increased from 0 to 1, 10, 25, 50 and 100 mM for alginate capped silver nanoparticles. It can be seen that the kinetic of adsorption initially increased from 0 mM NaCl to 1 mM NaCl but further increase in ionic strength led to a decrease in nanoparticle adsorption.

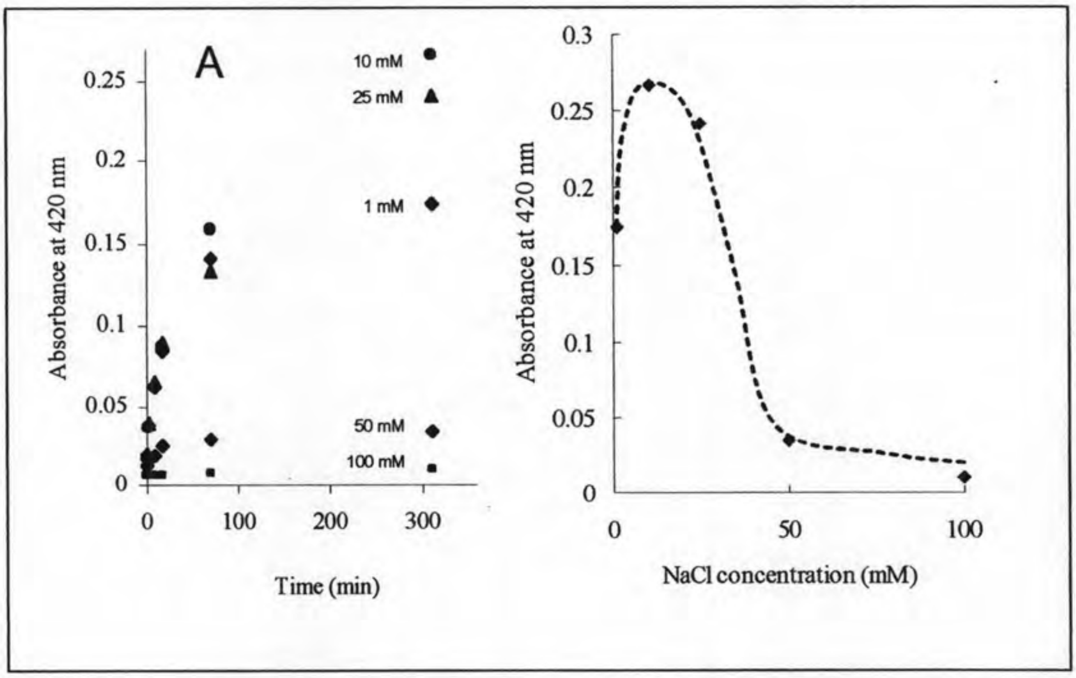


Figure 4.17: (A) Absorbance of alginate capped silver nanoparticle thin films prepared from different NaCl concentrations (0, 1, 10, 50, 100 mM). (B) Absorbance of the monolayer film used in (A) after 300 min as a function of the NaCl concentration.

The initial increase in saturation can be explained by a decrease in electrostatic repulsion of the nanoparticles adsorbed onto the surface. The salt ions play a screening role which cancel the repulsion of the nanoparticles having the same charge and therefore, decrease the bjerum length. The decrease in repulsion between adsorbed particles led to an increase in packing of particles and therefore, more efficient adsorption of the particle as it can be seen by an increase in the saturation layer from 0 to 1 mM. For salt concentration between 1 and 10 mM, a slight apparent decrease in adsorption is probably due to a slower kinetic as the driving force for complexation decreased due to the increased ionic strength of the solution. If more time was given, the 10 mM NaCl solution would obtain a higher final packing efficiency. When further increasing NaCl concentration from 10 mM to 25 mM and 100 mM, the adsorption of silver nanoparticles appeared very slow. This slow deposition process is to correlate with a solution which appears turbid. The increase in turbidity is due to the precipitation of the nanoparticles in higher NaCl concentrations. The precipitation occurred when the repulsion between colloids in suspension became smaller that the gravitational force. The decrease in repulsion was again due to the screening effect provided by NaCl ions.

4.4.4 Effect of the competitive adsorption

One of the interesting and puzzling observations in this series experiments is to explain why the nanoparticles capped with higher polyelectrolyte concentrations did not adsorb at the interface. This can be seen when comparing the adsorption kinetic of a nanoparticle solution prepared in the presence of a 10 mM polyelectrolyte solution with a solution prepared with 0.1 mM polyelectrolyte. The 10 mM solution led to the adsorption of a slightly yellow colored film whereas the 0.1 mM solution gave an intense yellow, almost orange film. These differences in absorbance can be seen in Figure 4.18. The adsorbed monolayer film display different absorbance yet the solution shown in Figure 4.3 display similar absorbance.

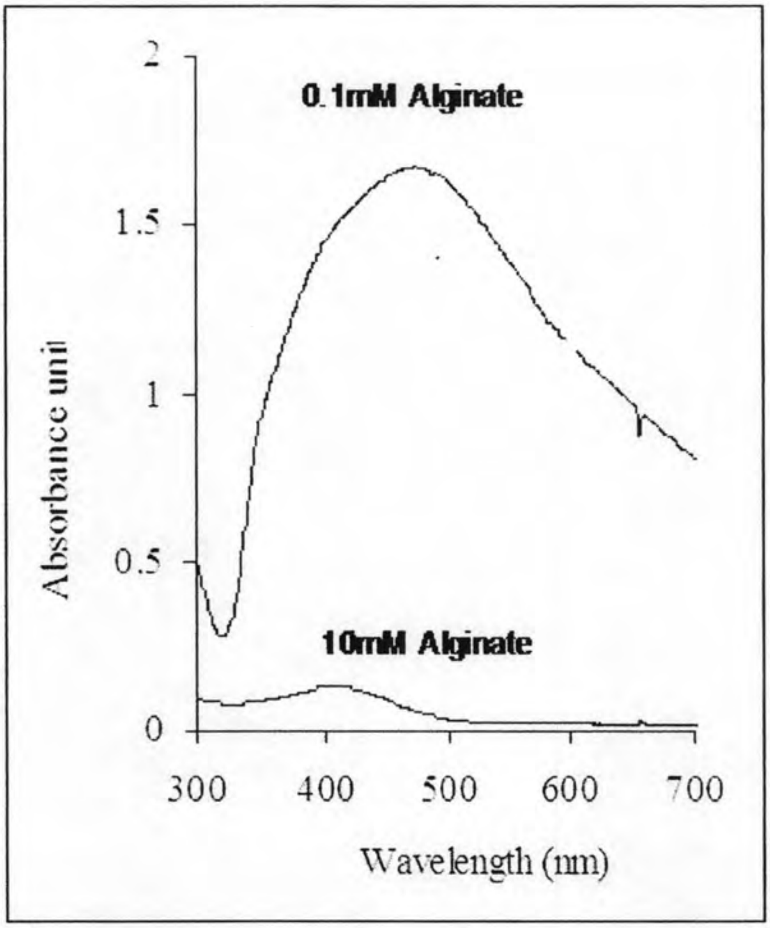


Figure 4.18: UV-Vis spectra of alginate capped nanoparticles thin film prepared from silver nanoparticles solution capped with 0.1 mM or 10 mM Alginate.

Although it is difficult to find justification to the difference in absorbance, when studying the whole UV-Vis spectra including the UV region around 200 nm a striking feature can be seen considering that the 200 nm wavelength include the polyelectrolytes absorbance. Shown in Figure 4.19 are the absorbance spectra of two silve nanoparticles monolayer films prepared from nanoparticles capped with either 10 mM alginate or 0.1mm alginate. The interesting part in these spectra is the relative absorbance increase between the 200 nm and the 400 nm peak. In the case of the 0.1 mM solution (plot A) the peak corresponding to the silver LSPR is greater than the UV peak corresponding to the alginate polyelectrolytes. This is not the case in the next plot (plot B) of the 10 mM alginate solution which shows a large alginate peak when compared with the silver peak.

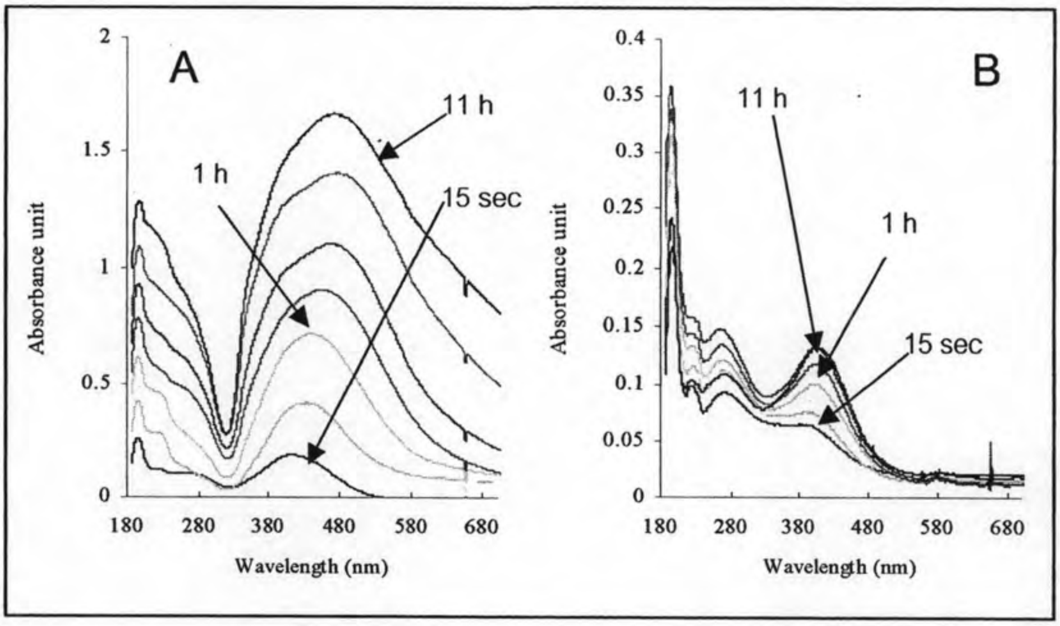


Figure 4.19: Changes in absorbance of a glass slide coated with a monolayer of silver nanoparticles prepared in presence of either 0.1 mM (A) or 10 mM (B) alginate concentration.

In order to more clearly seen the relative height of each peaks, the relative peak height was plotted for each solution as a function of the deposition time and shown in Figure 4.20. It can be seen that the difference in peak height is reversed from the 0.1 to the 10 mM solutions. Also the difference in peak height is greater in the case of the 10 mM solution suggesting that a greater fraction of polyelectrolytes adsorb onto the surface to the detriment of the nanoparticles. The excess polymer sticking onto the surface is probably due to unreacted polyelectrolytes which were mixed in solution with silver nitrate.

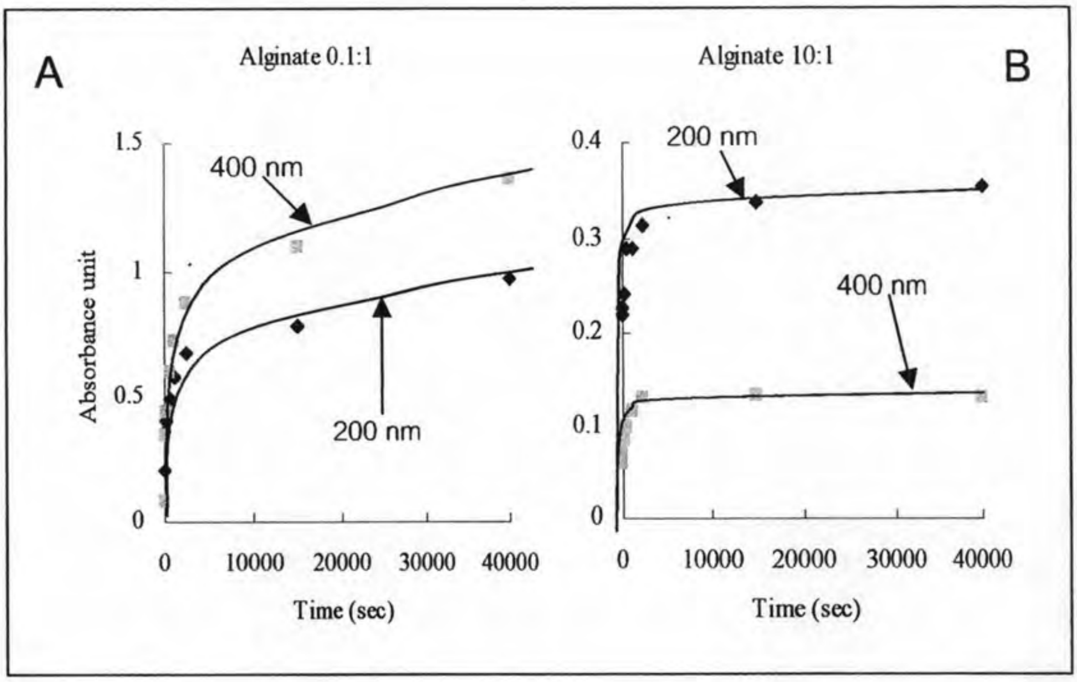


Figure 4.20: Plot of the peak intensity at different wavelength (200nm and 400nm) of monolayer films of silver nanoparticles prepared in presence of 0.1 mM alginate (A) or 10 mM (B).

Another point of interest appears when plotting the ratio of the peak height for each kinetic of adsorption. It can be seen in Figure 4.21 that the peak ratio is always greater in the case of the 10 mM but also that early stage of the adsorption the ratio is even greater suggesting that in both case, polyelectrolytes always stick faster than nanoparticles. The differences in hydrodynamic volume can be used to justify the differences in adsorption kinetic. The competitive type of adsorption depicted is of great interest and means that depending on the species present in solution, mixed adsorption can be obtained. Further development of the competitive adsorption could be developed and blended layers could be designed having interesting mixed properties. In conclusion, it is the competitive adsorption between excess polyelectrolytes and silver nanoparticles which prevented the adsorption of the nanoparticles in monolayer film when the particles were prepared from the 10 mM alginate solution. Similar behavior was obtained when excess polyelectrolytes was added to a solution of nanoparticles prepared from 0.1 mM alginate which further confirm the competitive adsorption between polyelectrolytes and nanoparticles.

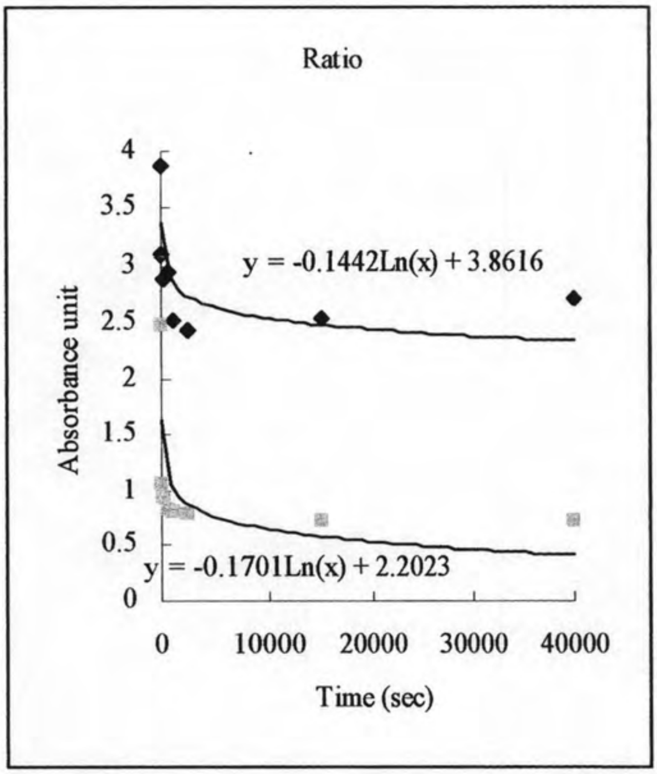


Figure 4.21: Peak ratio between absorbance at 200 nm and absorbance at 400 nm of silver nanoparticle monolayer thin films prepared from 10 mM of alginate (◊) and from 0.1 mM of alginate (□) solutions.

4.4.5 Morphology of silver nanoparticle monolayer

Atomic force microscopy was used to study the adsorption of silver nanoparticles onto a glass slide which had been coated with a 3 layers PDADMAC/PSS polyelectrolyte multilayer. The objective of this study was to investigate if the nanoparticles would assembled themselves into a monolayer onto the surface or if a stacking effect would occur leading to a large increase in thickness. AFM is the only

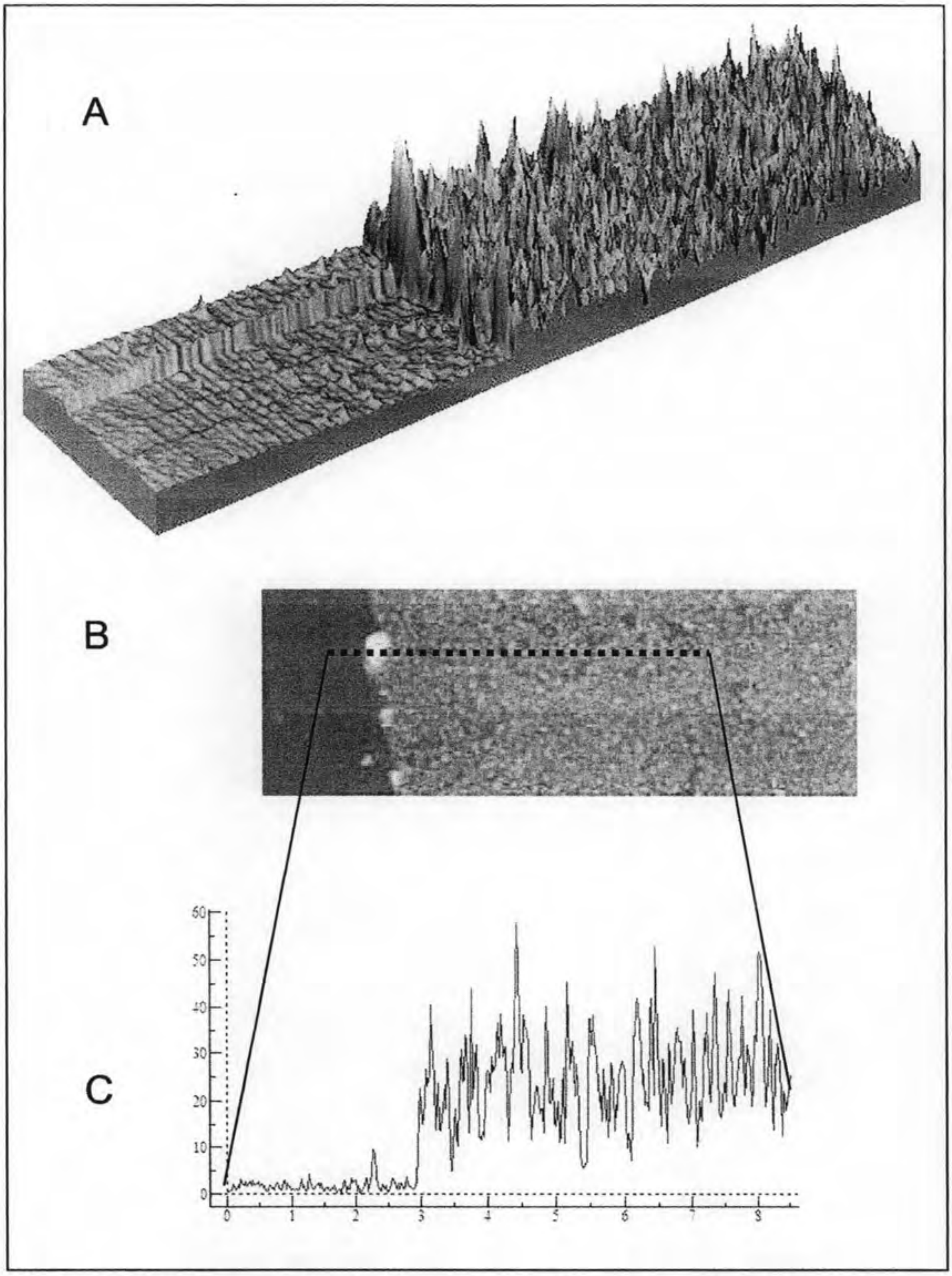


Figure 4.22: AFM image of the 0.1:1 alginate capped nanoparticles monolayer film surface. A: 3D view B: original view C: depth profile of the film.

instrument which can very efficiently and simply probe surface of the sample in order to study the type of monolayer formed. Yet because the AFM only probe the surface of the sample, in order to obtain information about the thickness of the nanoparticles layer, a scratch should be done with a sharp too in order to create a step edge. Then the AFM tip can be place on the edge and an AFM image of the cross section can then be taken for analysis [79].

From Figures 4.22 (B) and (C), the profile of the step edge reveals that the layer of adsorb nanoparticles posses in fact a thickness equivalent to the diameter of the nanoparticles. From Figure 4.22 (C) it can be seen that the step height from the scratch to the film increase from 2-3 nm to 5-50 nm. Since nanoparticles have been shown to have a particles size of around 30-40 nm this cross section suggest that nanoparticle adsorb simply at the surface in single layer fashion. This confirms that the nanoparticle adsorption occurred through monolayer formation only and that there was no stacking of the nanoparticles. Based on these results the UV-Vis absorbance kinetic study can be seen as the kinetic of adsorption of a monolayer.

4.5 Characteristics of alginate capped silver nanoparticle thin films

The layer-by-layer technique described in Chapter 2 was used for the assembly of silver nanoparticles thin films. This technique is described in the literature as polyelectrolytes multilayers thin films are based on the sequential adsorption of oppositely charged species. Based on electrostatic attraction between oppositely charges species, a film can be built with desired thickness by control over the number of dipping cycles. Using this technique, silver nanoparticles were assembled into thin films with polycationic PDADMAC. Shown in Figure 4.23 is a drawing which illustrates the thin film growth process based on the layer by layer deposition of silver nanoparticles but not include the rinsing steps. The rinse steps are fundamental as they ensure that any polyelectrolyte or nanoparticles which do not take part in the overcompensation phenomenon are removed. Since the adsorption due to complexation is thermodynamically stable, no desorption of any species should be observed at this step.

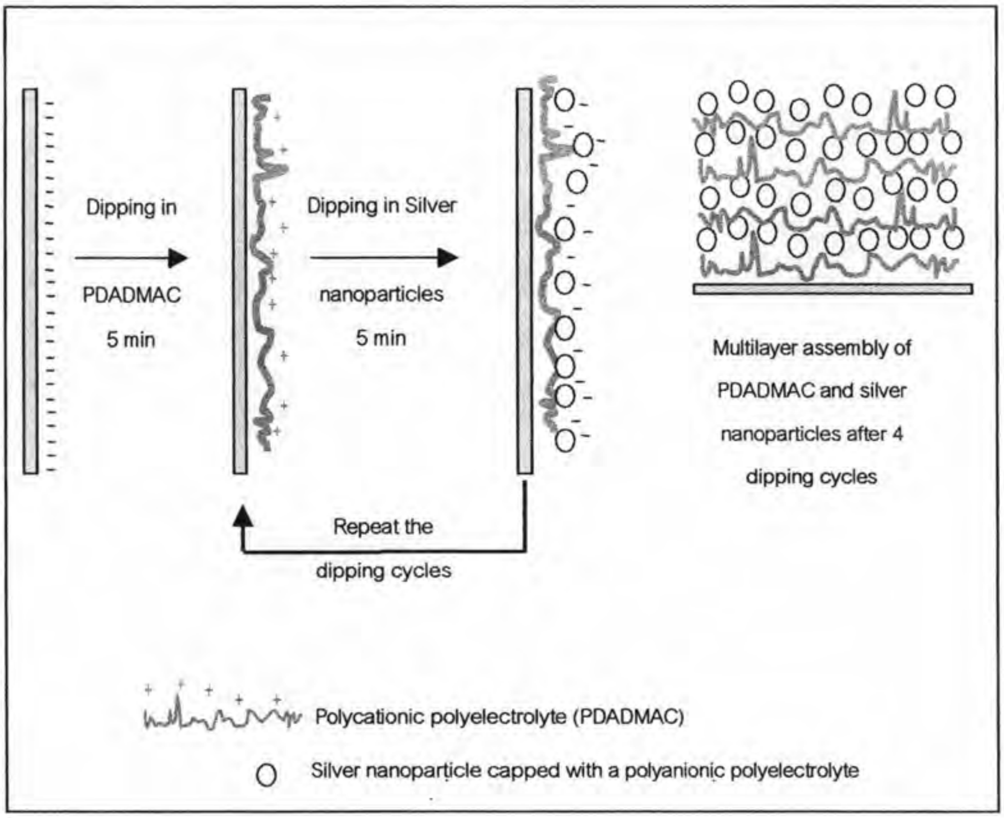


Figure 4.23: Diagram depicting the steps used in the layer-by-layer deposition of silver nanoparticles with PDADMAC.

4.5.1 Effect of the capping agent ratio on the growth of nanoparticle thin films

Figure 4.24 shows the changes in absorbance as a function of the number of deposited layers for silver nanoparticles prepared in the presence of 0.1 mM of alginate. As reported in previous published work, UV-Vis spectroscopy can be used to monitor the growth of the film due to the deposition of nanoparticles, which absorb the light. It is expected that in early number of layers from 1-10 when using polyelectrolytes, the increase in thickness would not be constant and would display a shape similar to that shown in Figure 2.11. In this work published by Schlenoff the non linear growth of the initial layer was justified by a wall effect due to the limited diffusion of the polyelectrolyte by the substrate. In the present case because nanoparticles are not expected to diffuse as much as polyelectrolytes, an immediate linear growth should be observed. As seen in

Figure 4.25, the linear growth can be seen in each film built from solutions of increasing alginate content.

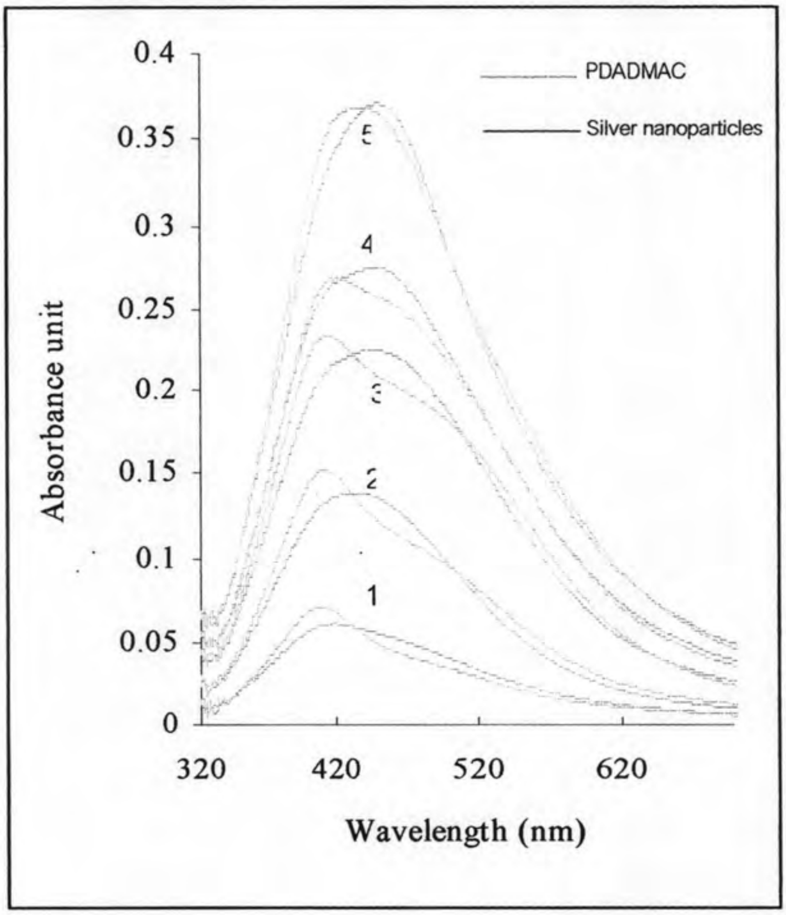


Figure 4.24: UV-Vis spectra of PDADMAC and silver nanoparticle multilayer thin films. The number 1, 2, 3, 4 and 5 correspond to the increasing number of deposited bi-layers.

As expected in the layer-by-layer deposition process, UV-Vis spectra in Figure 4.24 an increase in absorbance due to the deposition of the nanoparticles. Because UV-Vis absorbance is proportional to the concentration of species located in the path of the light beam, the accumulation of nanoparticles on the thin film leads to an increased in absorbance. Nevertheless the increase in absorbance should only be observed for the dipping steps involving the deposition of silver nanoparticles and not the deposition of PDADMAC which does not absorb light in this wavelength range. This can be seen by the fact that UV-Vis spectra show an overlap of the peak for every other layer. An interesting shift in absorbance is to be observed from the films which have nanoparticles as a top layer or have PDADMAC as a top layer. The film with nanoparticles on top appears to be more red shifted which suggest a more hydrophobic character due to metal particles present at the surface of the film. Upon complexation between the top layers and the next PDADMAC layer, the formation of a more hydrated layer and hydrophilic characters is obtained which induce the red shift on each spectra.

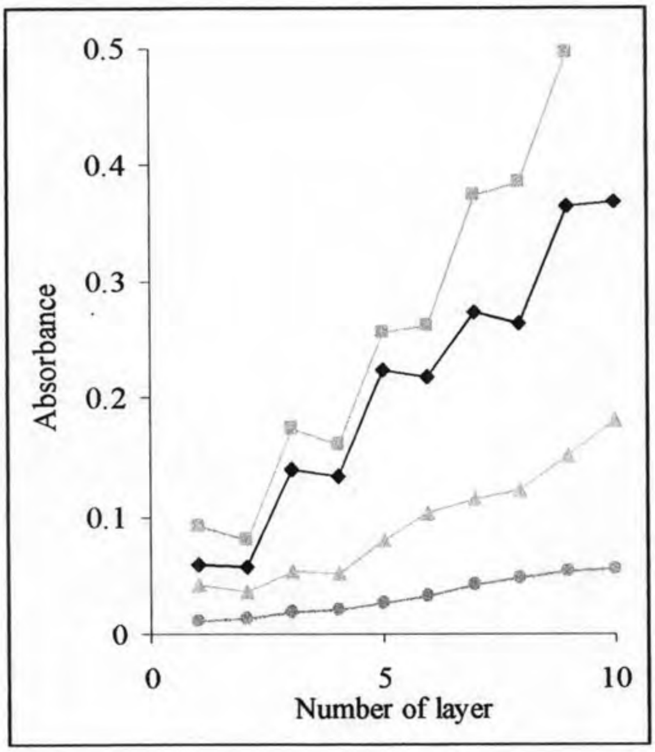


Figure 4.25: Plot of the changes in λ_{max} absorbance of a PDADMAC and nanoparticles thin film prepared using different alginate concentration (diamonds = 0.1 mM; squares = 0.5 mM; triangles = 1 mM and circles = 5 mM).

Shown in Figure 4.25 is the layer by layer growth of the nanoparticles thin films as a function of the polyelectrolyte concentration used to prepare the silver nanoparticles. It can be seen that the nanoparticles deposited from the 0.5 mM alginate content grow faster than the one assembled from solutions containing 0.1 mM alginate. The lower growth rate is due to a slower kinetic of adsorption and therefore a decrease in changes in absorbance after each dipping steps. The slower kinetic is probably due to the fact that when the capping agent is too dilute as in 0.1 mM alginate the binding force of the nanoparticles onto the oppositely charged surface is lower and therefore might have a higher desorption rate. In other words the nanoparticles having a lower capping agent content are less sticky to the surface and therefore do not assembled as well.

4.5.2 Effect of the capping ratio on the mechanical properties of the film

The effect of the capping agent molar ratio used in the preparation of the nanoparticles onto the final mechanical strength of the thin film was evaluated by using the nanoindentation technique. The thin films were prepared from silver nanoparticles capped with 10 mM, 5 mM, 1 mM or 0.5 mM of alginate and then indented with the AFM diamond tip. The data from the film prepare from 0.1mM could not be used because the film was too rough leading to high uncertainty on the depth measurements. Because the indentation print left in the materials is the results of the bending of the stainless steel cantilever ,holding the diamond tip, and the displacement of the diamond tip in the sample, a blank measurement must be taken in order to asses the bending properties of the cantilever. Shown in Figure 4.26 is an AFM image of the indentation of the diamond tip in a silicon wafer. The silicon wafer was chosen as a blank because it is expected to be much harder than the nanoparticle films. From the deflection data it is possible then to obtain the displacement of the AFM piezoelectric cell for each applied voltage. Table 4.1 displays a summary of the displacement values obtained for the blank displacement test and the thin film test.

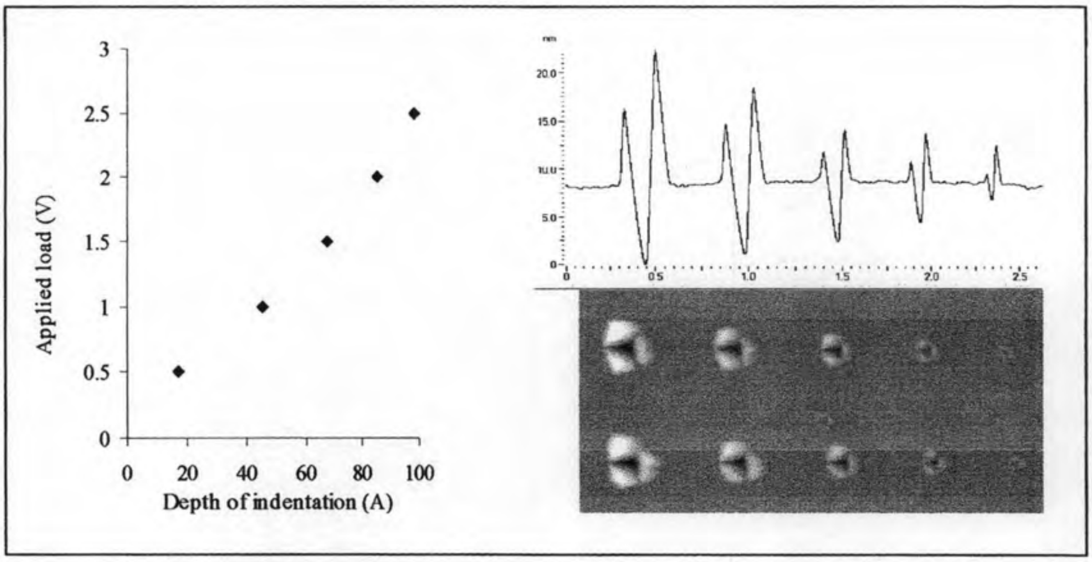


Figure 4.26: (A) Plot of the indentation depth in silicon as a function of applied voltage. (B) Depth profile of the indent as a function of the applied voltage from left to right (2.5, 2, 1.5, 1, 0.5 V). (C) AFM image of the indentation. Indentations are 500 nm apart.

Table 4.1: Indentation data for silver nanoparticle thin films

Capping ratio Alginate:$AgNO_3$ (mM)	load (V)	total displacement (nm)	Tip bending (nm)	indentation (nm)
0.5:1	0.5	100	60.9	39.1
0.5:1	1	230	124.2	50
0.5:1	1.5	241	182.1	58.8
0.5:1	2	311	238.8	72.1
0.5:1	2.5	402	297.8	104.1
1:1	0.5	100	60.9	39.1
1:1	1	173	124.2	48.7
1:1	1.5	286	182.1	58
1:1	2	304	238.8	65.1
1:1	2.5	382	297.8	84.1
5:1	0.5	93	60.9	32.1
5:1	1	164	124.2	39.7
5:1	1.5	230	182.1	47.8
5:1	2	294	238.8	55.1
5:1	2.5	361	297.8	63.1
10:1	0.5	90	60.9	31
10:1	1	160	124. 2	37
10:1	1.5	230	182.1	47.8
10:1	2	301	238.8	62.1
10:1	2.5	368	297.8	70.1

Seen in figure 4.27 is an AFM image of the indentation left by the diamond tip onto the sample. The depth values have been reported in table 4.1. From these results it can be seen that the value of the depth of the indentation is higher in the case of the 0.5 mM (100 nm) when compared to 5 mM (63.1 nm) which suggest that the higher polymer content is harder.

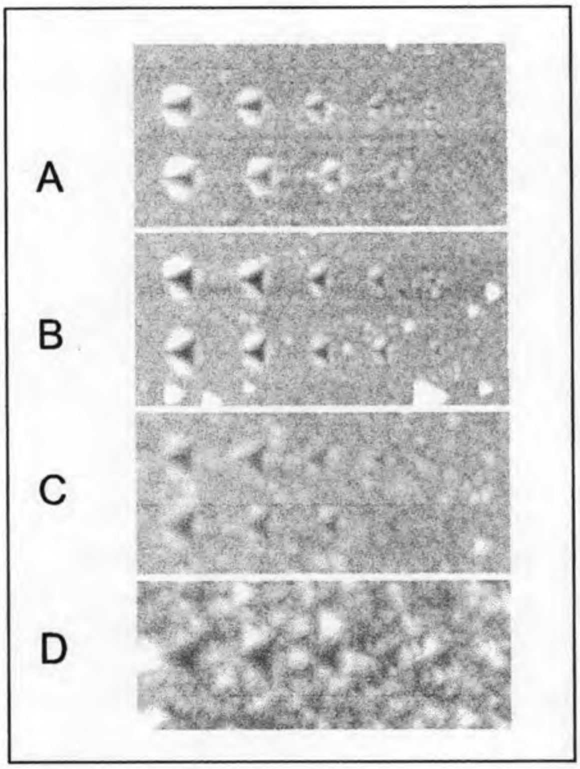


Figure 4.27: AFM images of the indentation of 4 nanoparticle thin films prepared from alginate capped nanoparticles at the concentration of 0.5mM (A), 1mM (B), 5mM (C) and 10mM (D).

When plotting the changes in displacement as a function of the applied load (Figure 4.28) the coatings display different response to the applied load. Results show there is a correlation between the hardness of the film and the amount of alginate used in the preparation of the nanoparticles. When the alginate content was increased from 0.5 mM to 5 mM the hardness was increased as it can be seen from the lower displacement but further increased of the alginate content to 10 mM led to a decrease in hardness. Although the hardest coating was prepared from 5 mM, these results have to be analyzed with caution due to the co-adsorption phenomenon described in section

4.4.4. Further studies will be needed to clarify whether the loss of hardness is due to the co-adsorption phenomenon or a change in surface coverage of the nanoparticles.

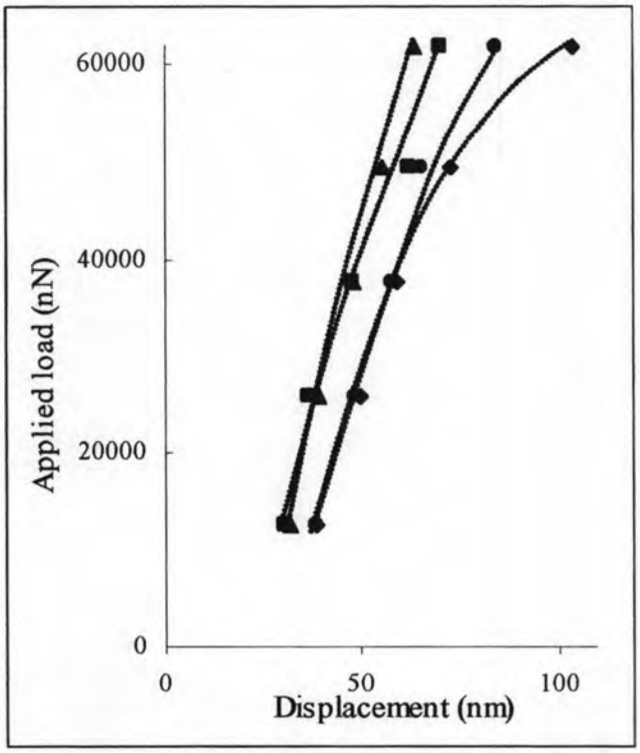


Figure 4.28: Plot of the nanoindenter as a function of applied load for the films prepared from nanoparticles capped with 0.5mM alginate (diamonds), 1mM alginate (circles), 5mM alginate (triagles) and 10mM alginate (squares).

4.6 Sensing properties of silver nanoparticle films toward ethanol and methanol

In the previous section, silver nanoparticles assembled into thin films showed some interesting sensing properties toward ethanol. As shown in figure 4.10 of this chapter, silver nanoparticles in solution display vivid color change when exposed to different solvent probably due to changes in the dielectric constant of the nanoparticle surrounding. Yet once assembled it is necessary to confirm the sensing properties of the nanoparticles by evaluating their optical response to various organic compounds.

4.6.1 Sensing of the thin films toward ethanol in water

Using the layer-by-layer technique, 20 layers of silver nanoparticles and polycationic PDADMAC were sequentially deposited. The electrostatic interactions between oppositely charged polyelectrolytes allow the fabrication of uniform films. The resulting film formed by the successive deposition of 20 layers of PDADMAC and silver nanoparticles capped with alginate displayed and interesting color switch depending on the surrounding solvent. The film appeared yellow when dipped in water but changed to a strong orange-red color upon drying or dipping in more polar solvent such as ethanol. The color shift between yellow and orange was found to be reversible and very fast. This color switch suggested the potential development of a sensor or optical device which could be trigger by the changing surrounding organic compounds such as an ethanol/water mixture. In order to characterize the sensing properties of the film, the changes in absorbance when exposed to increasing ethanol content (0, 20, 40, 60, 80 and 100% ethanol in water) were monitored and plotted in Figure 4.29. It can be seen that the characteristic yellow peak centered at 400 nm gradually shift to a peak centered at 545 nm as ethanol content is increased from 0 to 100%.

The color change is due to the variation in dielectric constant of the surrounding of the silver nanoparticles upon exposure to less polar solvent. Reported calculations from Mie theory confirm such behavior of a red shifted plasmon absorbance band of the nanoparticles upon exposure to less polar solvent. The 550 nm wavelength was used because it presents the widest range change in absorbance. The corresponding absorbance values at 550 nm are shown in the cartouche Figure 4.29.The kinetic of the nanoparticles' color change was found to be extremely fast which suggest that these films could be used as optical switches.

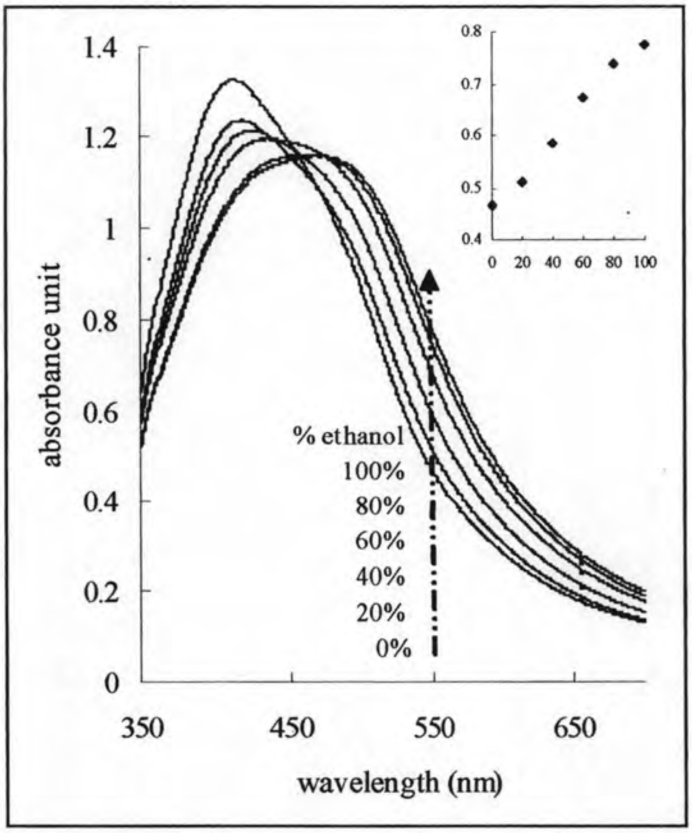


Figure 4.29: UV-Vis spectra of a 20-layered PDAMAC and 0.1:1 (alginate:AgNO$_3$) silver nanoparticle film as a function of the ethanol content.

To characterize the fast switching of silver nanoparticle film, a simple homemade light sensor similar to that already reported in the literature [25] was used. The film was placed in a flow through cuvette and exposed to solutions of either 100% ethanol or pure water. As seen on Figure 4.30, the color switch is fast and occurs in less than a second since no intermediate point could be recorded with a sampling rate of 1 second. Shown on the graph is a section of cycling test but up to 100 cycles were performed with similar efficiency and switching speed which suggest that the coating is stable.

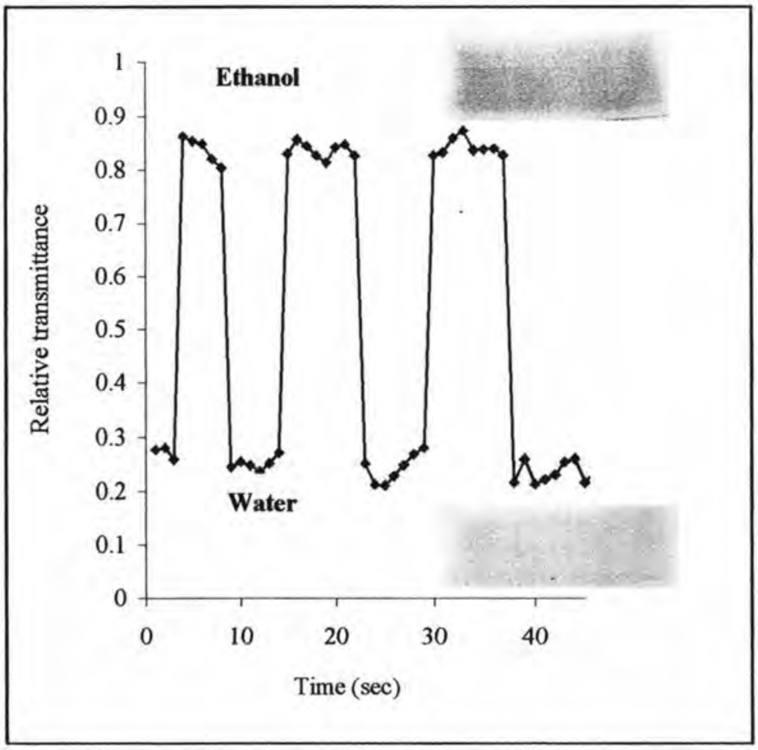


Figure 4.30: Changes in transmittance of the 0.1:1 (alginate:AgNO$_3$) silver nanoparticle film when exposed to either water or 100% ethanol solution. The sampling rate used in this experiment is 1sec per data point.

4.6.2 Sensing properties of the thin films toward methanol

Figure 4.31 shows, the sensing response of the film to both ethanol and methanol are shown. The two set of spectra display similar features such as a red shifted absorbance due to the increase in dielectric of the surrounding medium. As stated in chapter 2, the changes in dielectric will influence the optical properties of the film. Yet when the cumulative changes are plot together, no clear difference can be concluded between ethanol and methanol. Water has a dielectric constant of 80 but methanol and ethanol have dielectric constant of 33 and 24 respectively. The small difference in dielectric between these two organic compounds are difficult to elucidate. In the next section, the coating of the silver nanoparticles thin film will be performed in order to induce selectivity toward the detection of methanol and ethanol.

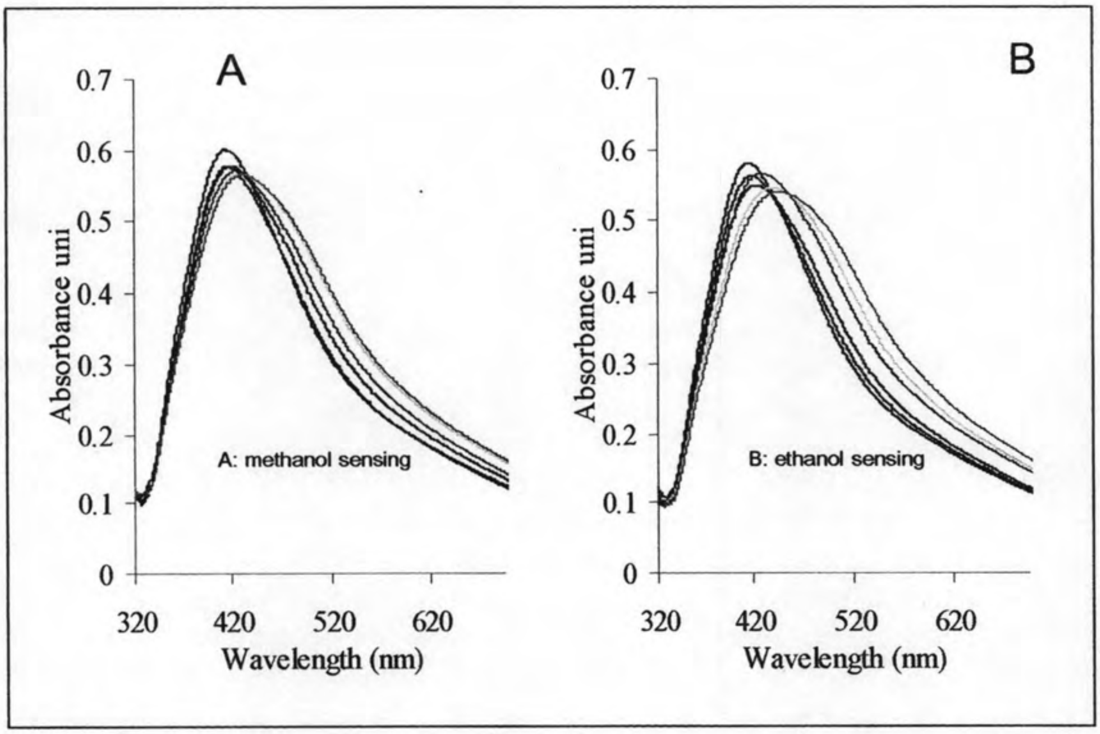


Figure 4.31: UV-Vis spectra of 0.1:1 (alginate:AgNO$_3$) silver nanoparticle thin films response to either increasing concentration of methanol of increasing concentration of ethanol from 0, 20, 40, 60, 80, 100% v/v volume solvent in water

Figure 4.32 compile the changes in absorbance at 550 nm as a function of methanol and ethanol content. It can be seen that very little difference can be made between each solvent as the plot of their sensitivity almost overlap.

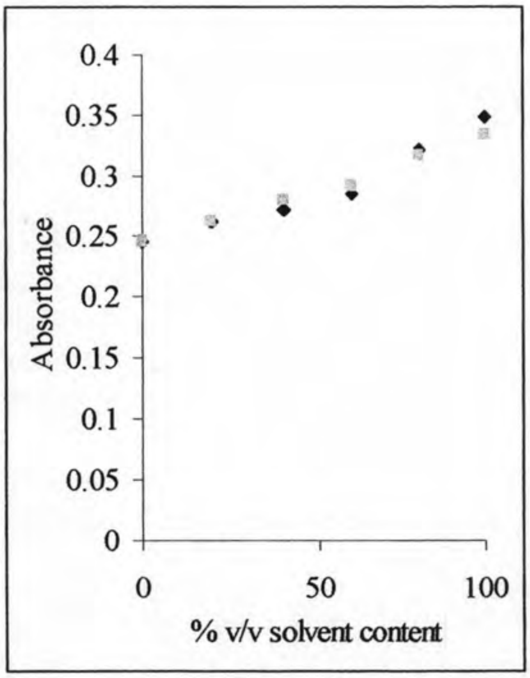


Figure 4.32: Plot of the changes in absorbance of 0.1:1 (alginate:AgNO$_3$) silver nanoparticle thin film at 550 nm when exposed to increasing content of ethanol (diamonds) and methanol (Squares) in water.

4.6.3 Detection of ethanol from methanol

An interesting point in these experiments was to intent the selective sensing of ethanol from methanol and their mixture with water. The detection of ethanol from methanol was also intended and the results of the sensing experiment are plotted in Figure 4.33. It can be seen again on the UV-Vis spectra and the plot of the absorbance at 550 nm that almost no distinction can be made from the spectra of the mixtures of solvents. The fact that the film cannot make any difference between ethanol and methanol is due to the fact that they have a very close dielectric constant and therefore induce similar spectral shift from the silver nanoparticle thin films.

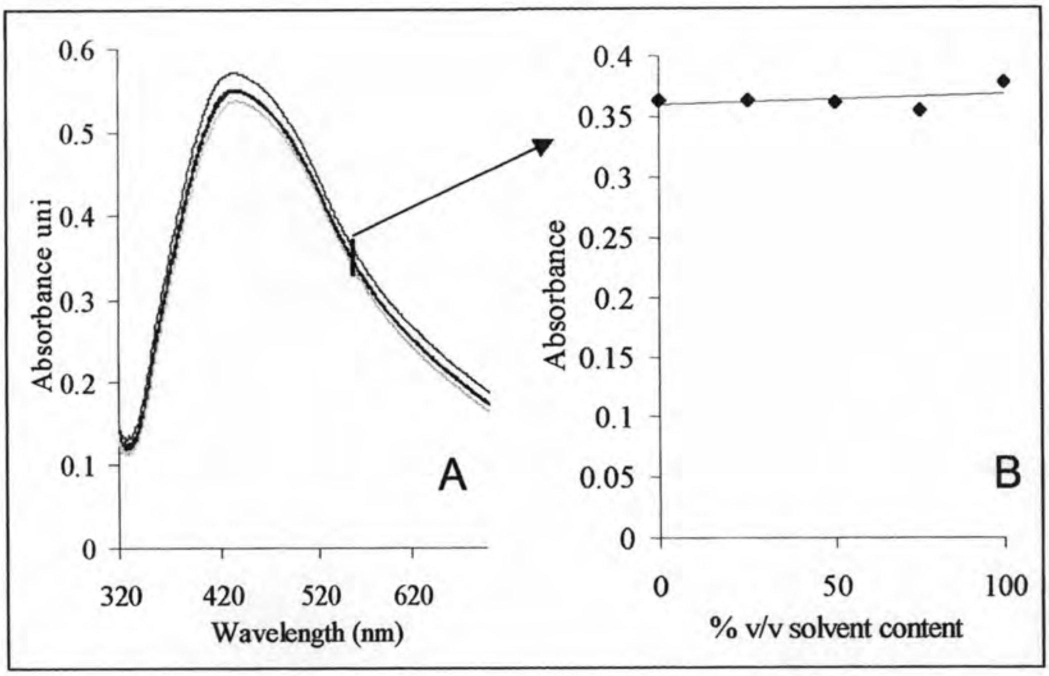


Figure 4.33: (A) UV-Vis absorbance spectra of 0.1:1 (alginate:$AgNO_3$) silver nanoparticle thin film exposed to increasing concentration of ethanol in methanol. (B) Plot of the absorbance value at 550 nm for the corresponding spectra.

4.7 Effect of the nanoparticle thin film structure on the sensing properties

In this section, the changes in sensitivity of the silver nanoparticles thin films will be discussed. The original film refers to the simple alternating deposition of PDADMAC and silver nanoparticles in a layer-by-layer fashion. Three types of modified films have been prepared and include the X-Y spacing of nanoparticles, the Z spacing with intercalated layers and finally the surface modification of the sensor surface by adsorption of a polyelectrolytes layers.

4.7.1 X-Y spacing of nanoparticles thin films

X-Y spacing of the nanoparticles was intended by co-adsorption of metallic nanoparticle with polyelectrolyte and by intercalating multilayers in between assembled nanoparticle layers. This experiment could be summarized as follow in the diagram shown in Figure 4.34 where the packing factor of the nanoparticles was decreased. This technique had for objective to tune the optical properties of the film but have not been successful in improving the detection of organic compound from the film. This failure in detection is due to the fact that the highly hydrophilic character of the polyelectrolytes used gave a very high content of water in the thin film. This led to the appearance of a yellow colored thin film in both X-Y and Z assembly. Due to the yellow color, the optical switch between orange/red and yellow upon changes in solvent quality was not observed. This lack of color switch renders the films useless for organic compounds sensing but could be useful in antimicrobial applications where hydrated coating could release silver ions which are known for their antimicrobial properties.

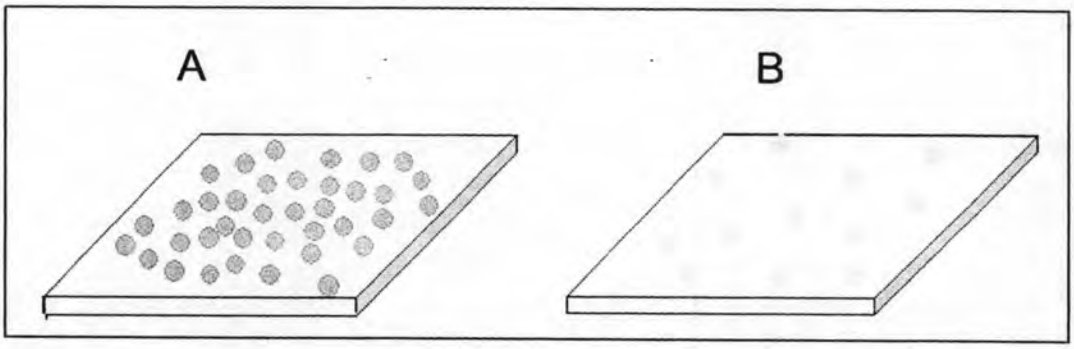


Figure 4.34: Two different packing models of silver nanoparticles at the surface of the layer

4.7.2 Z spacing of silver nanoparticle thin films

The z spacing of silver nanoparticles was obtained by intercalating multilayers in between assembled nanoparticle layers. As shown in Figure 4.35, the original (PDADMAC/Nanoparticles)$_x$ sequence for the deposition of x bi-layer was replaced by the intercalated sequence (PDADMAC/PSS/PDADMAC/Nanoparticles). In this way, 3 layers of PDADMAC /PSS/ PDADMAC were intercalated between each nanoparticle layers.

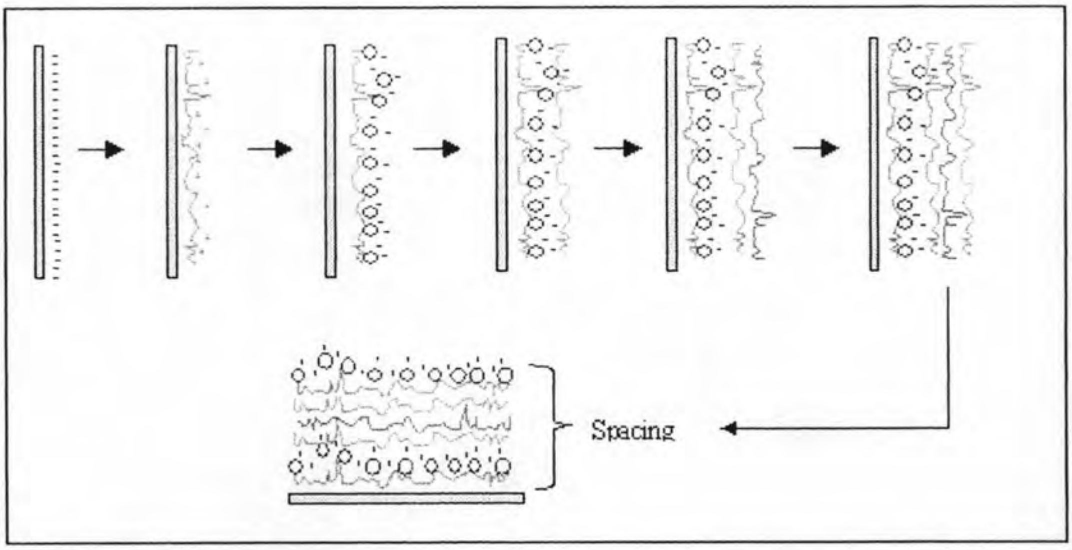


Figure 4.35: Diagram of the intercallation of a 3 layer coating in between the two silver nanoparticle layers

The prepared film appears to have a more yellow color than the original film which suggests a more hydrophilic character. This can be confirmed in Figure 4.36 as the spectrum of the film present more blue shifted and narrower UV-Vis absorbance when compare to the original film. On the same Figure 4.36 the sensing properties of the two films are compared. While the original film displays different responses as a function of the surrounding solvent, the intercalated film does not show any difference in spectra. This again, suggests a more hydrophilic character which tends to repel the organic compounds from the bulk phase of the film. The intercalation of PE layers was intended to modify the hydrophobic/hydrophilic nature of the composite film and tune its response to various solvent. The conclusion of this experiment is that the over-expressed hydrophilic nature of the film prevents any solvent to penetrate and therefore make the film useless for sensing applications. Nevertheless, other type of PE (more hydrophobic) could be used in the film and might provide a different response.

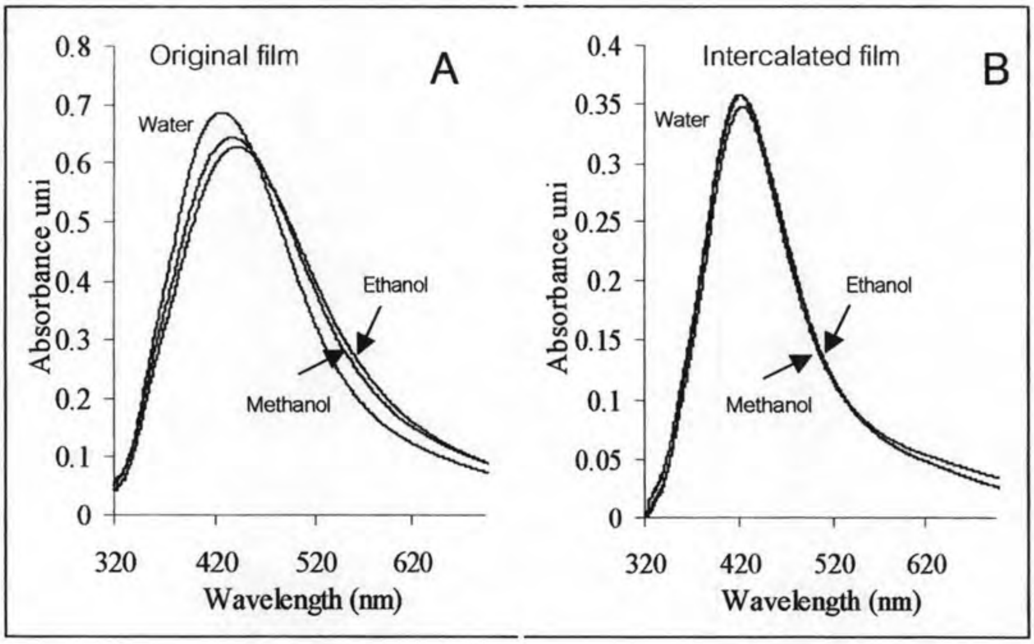


Figure 4.36: (A) UV-Vis absorbance spectra of 0.1:1 (alginate:$AgNO_3$) silver nanoparticles thin film exposed to water, ethanol and methanol. (B) UV-Vis spectra of 0.1:1 (alginate:$AgNO_3$) silver nanoparticles thin film modified with 3 intercalated layers of PDADMAC and PSS, exposed to water, ethanol and methanol

4.7.3 Surface modification of the nanocomposite sensing film

4.7.3.1 Effect of the number of layers

In the last part of this work, the objective was to modify the surface of the sensor in order to change its optical response. In this part changes in response from the alginate sensor will be evaluated against methanol and ethanol in order to see if it is possible to detect ethanol from methanol. The surface of the sensor was coated with various numbers of layers assembled from PDADMAC and PSS. The diagram in Figure 4.32 summarizes the objective of the coating and in picture A the sensor film is not able to differentiate between ethanol and methanol. Show in Figure B is the effect of the coating with a PEM which prevent the migration of one organic compound over the other and therefore allow the sensor to be used in detection of a specific solvent mixture.

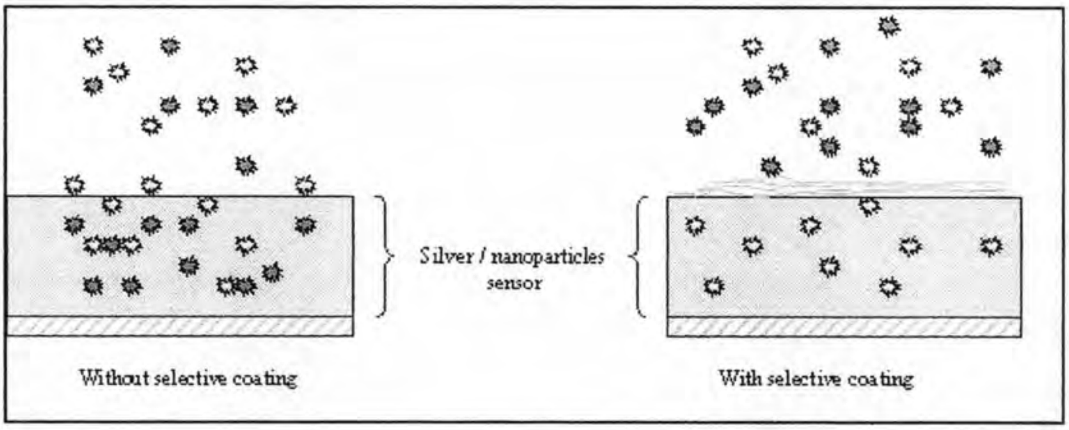


Figure 4.37: Surface modification of the composite thin film for selective sensing

Figure 4.38 shows the changes in methanol sensing as a function of the number of coated layers. It can be seen that while the first PDADMAC layer does not change excessively the sensing properties of the film, the deposition of the second and third layer already completely block methanol from permeating into the sensing film. It should be expected that the first layer could not block the methanol from diffusion since the layer would be rather thin. Under the buildup conditions (10 mM PDADMAC and 1M NaCl) the thickness of the layer would only be 10 nm. The coating layer acts as a selective filter which let water permeates through but repel methanol. The thicker the layer is the more efficient is the repulsion effect. Second and third layers show good repulsion and completely block the methanol from permeating in the sensing thin film which retains its yellow color. Bruening *et. al.* [141] already reported the use of PEM as selective filter in order to remove the organic compounds from water. To explain the selective permeation effect, they suggested that it is the dense electrostatic nature of the PEM which prevent the organic compound from permeating through. In their work they used PEM in nano-filtration application and were successful in separating ethanol from water after a single filter pass. Here also it is probably the electrostatic nature of the PDADMAC/PSS PEM

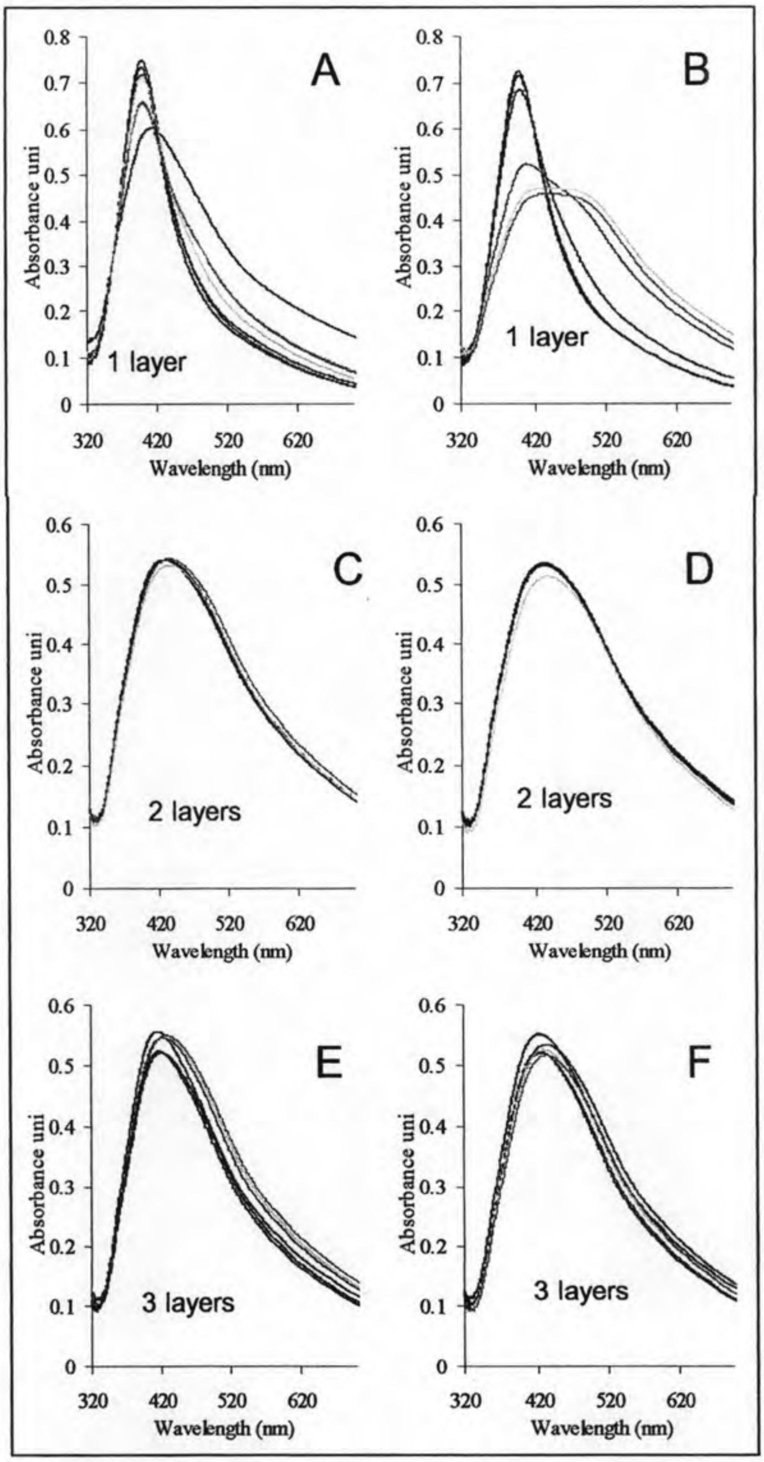


Figure 4.38: Absorbance of 0.1:1 (alginate:AgNO$_3$) silver nanoparticle thin films as a function of methanol content in water modified with 1 (A, B), 2 (C, D) and 3 (E, F) PEM layers of PDAD/PSS.

which repel the methanol contained in the water and lead to a lower methanol content in the PEM when compare to the methanol content in the solutions.

As mentioned in the introduction, it is the detection of methanol from ethanol which would be the ultimate challenge since these two organic compounds are very close in properties and structure. The work presented here could lead to the development of simple and efficient optical sensor based on nanocomposite film containing silver nanoparticles. As seen in Figure 4.38, the 3 layered coating is able to provide sufficient selectivity for the detection of ethanol from methanol. Seen in plot A Figure 4.38 the reader can see that although the signal from similar ethanol content decrease after the coating of the film, the sensor is still able to detect ethanol in the range 20% to 100%. On the other hand, when the same coating is exposed to increasing methanol content, the bare sensor give a similar response but the 3 layers coated sensor does not show any sign of methanol. This means that the coating completely blocked the diffusion of methanol. Because the three layers PEM coating is able to selectively block methanol from ethanol the surface modification of optical sensor by PEM is a very useful tool for the tuning of the sensing properties of this sensor.

4.7.3.2 Memory effect

An interesting phenomenon was observed when testing the sensitivity of the film toward ethanol and methanol. It appeared that the ethanol sensing properties where function of whether the last rinse was made in water or in methanol. In Figure 4.39 the sensor film is alternatively exposed to methanol or ethanol. The UV-Vis spectra on the left side do not show the expected plasmon shift when the film is dipped in 100 % ethanol solutions. The changes in absorbance at 550 nm plotted on Figure 4.39 right picture show only a small amplitude changes.

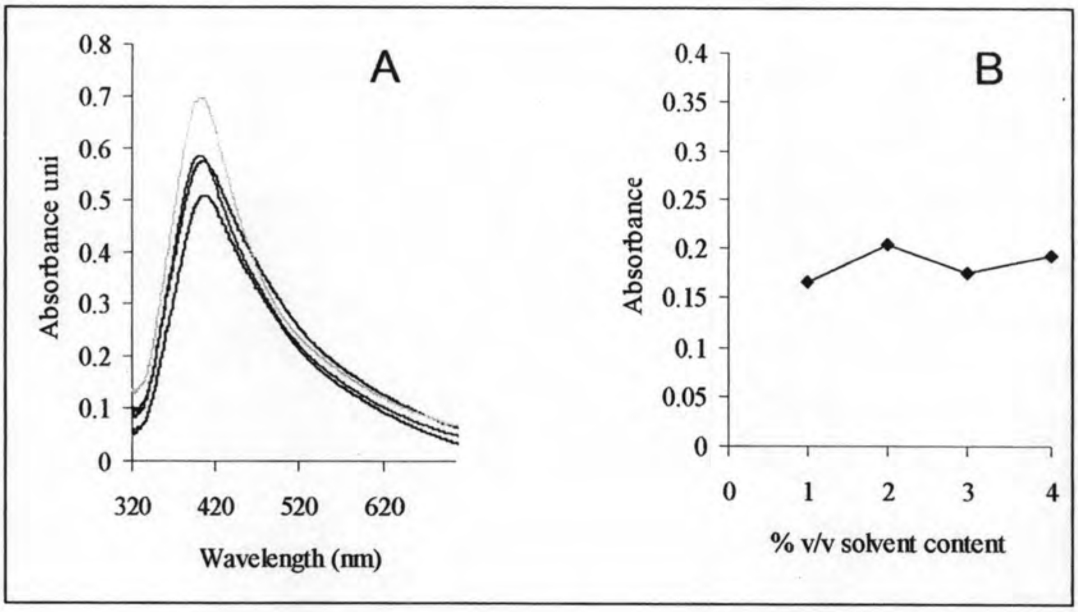


Figure 4.39: (A) UV-Vis absorbance spectra of a 3 layered intercalated 0.1:1 (alginate:$AgNO_3$) silver nanoparticles thin film exposed either solutions of ethanol or methanol. (B) Plot of the absorbance value at 550 nm for the corresponding spectra.

On the other hand when the same experiment was repeated by the sensing film was rinsed with water, the optical shift was then found to be those expected, in Figure 4.40, the large changes in plasmon band can be seen on the left image and the plot of the changes in absorbance at 550 nm also show large amplitude changes.

This memory effect due to the last rinse in water, methanol or ethanol could be due to the fact that the organic compound has a great affinity with the polyelectrolyte multilayer thin film. When the film was last dipped in methanol, the next rinse and dip in ethanol does not remove the trapped methanol which explains why the spectra are not shifted. In contrast when a water rinse is applied to the film, the methanol is removed and allows the ethanol to interact with the nanoparticles.

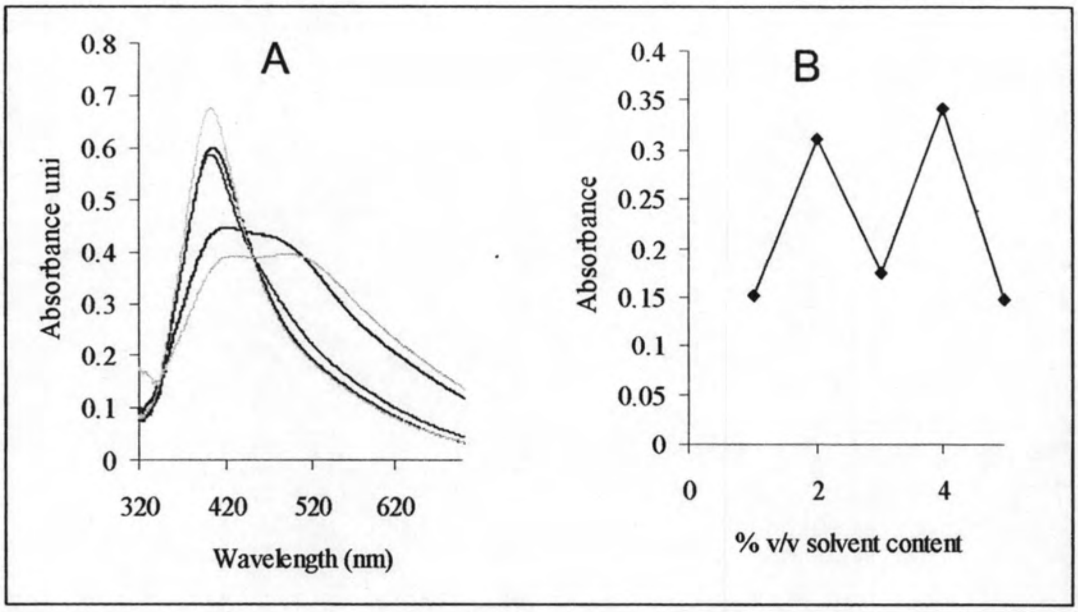


Figure 4.40: (A) UV-Vis absorbance spectra of a 3 layers intercalated 0.1:1 (alginate:$AgNO_3$) silver nanoparticle thin film exposed either solutions of ethanol or methanol. (B) Plot of the absorbance value at 550 nm for the corresponding spectra.