CHAPTER I

INTRODUCTION

Nanomaterials have received huge interest from the scientific community because of their unique properties. Due to the variety of functionalities, size, shape and chemistry found in nanomaterials, they have the potential to be used in nearly all fields of science and technology. Whether it concern catalytic nanoparticles, microstructured zeolites for energy storage or single wall carbon nanotubes for drug delivery, nanomaterials usually display superior properties than bulk material. Among the multitude of applications which have been suggested using nanomaterials, it is the sensing properties of nanomaterials which have been studied in this research. Due to their extremely high surface to volume ratio, nanomaterials have huge surface area and often have high reactivity, making them useful for sensing applications.

Sensors are needed everywhere in our society and need to be sometimes modified to match the new requirements of our fast growing economy. The recent development of bio-diesel and ethanol or methanol based fuel has lead to increase research in the production method of such alternative energy source. While production methods are being improved, the development of sensor to monitor the quality of such compound is of interest. The task of the sensor developed here is to be able to detect and quantify the presence of alcohols such as methanol, ethanol, and propanol in a given solution. This sensor could not only be used in the energy industry but also in the food industry for the online monitoring of for methanol in reaction vessel of alcoholic beverage. Later the sensor could be further developed and be used to identify the presence of organic compound such as pesticides in rivers. The selectivity and stability of the sensor was an important point to focus on during the development of the device.

Nanomaterials can be used as sensors based on different detection principles. The most commonly used takes advantage of the change in conductivity of an oxide layer upon adsorption of a target molecule. Wide ranges of sensor have been developed and the objective of this research has been to develop an optical based system. Although many other options exist, the optical method is very interesting because it can be easily miniaturized and interfaces with optical fiber for direct measurements. While many sensors are able to detect molecules and other organic chemical in the vapor form, fewer devices can be used in solution. For this reason the objective was to develop a sensor, which could function in liquid. Other systems have been proposed very successfully and concern the utilization of silver or gold nanoparticles which are well known for their characteristic color due to the surface plasmon absorbance band. Although they are usually used in solution, the sensing mechanism use in this research is be based on the immobilization of metallic nanoparticles onto a transparent substrate in the form of a thin film. The interaction between solvent/nanoparticles, solvent/film and nanoparticles/nanoparticles usually leading to a shift in position of the plasmon band of the nanoparticles. In this work it is this spectral shift as a function of the solvent quality and as a function of the chemistry of the metal polymer nano-composite thin film which was used to detect various compounds.

For the fabrication of the sensor, silver nanoparticles have been prepared and then assembled into thin films using the layer-by-layer (LbL) technique. Based on a simple dipping step, this LbL technique allows the fabrication of polymer nano-thin films and provides outstanding control over the final thickness and surface properties. Silver nanoparticles have been prepared using polyelectrolytes as capping agent in order to deposit them into thin films. The resulting thin films have been used as optical sensor for the detection of organic compound in water. The sensing properties of these films are based on the particular optical properties of silver nanoparticles which display an intense extinction around 400 nm. The spectral absorbance of the nanoparticles is strongly influence by the dielectric of the surrounding medium which occur when the nanoparticles are exposed to different compound. For the silver nanoparticles based sensing films, different architectures have been investigated. Firstly a basic alternating deposition of the silver nanoparticles with a poly-cationic polyelectrolyte was used to the preparation of the basic sensor. In second, the effect of in plane spacing of the nanoparticles as well as the Z (off-plane) spacing was studied. The objective was to modify the structure of the composite film and study its effect over the sensing properties. It was hypothesized that changing and tuning the spacing between particles could modify their response to various organic compounds. In the last part of the project, the sensing films were coated with an extra polymer thin film which acted as a selective barrier in order to improve the recognition toward ethanol and methanol.

The characterization techniques used in this project are to be separated into three parts. The first method concerns the study of the morphology of the prepared nanoparticles by Transmission electron microscopy (TEM) and UV-Vis spectroscopy. In a second part, once the nanoparticles were deposited into thin film as monolayer or multilayers, Atomic force microscopy (AFM) was used to monitor the film thickness and the packing of the nanoparticles at the surface of the substrate. Finally in order to evaluate the sensing properties of the films, UV-Vis spectroscopy was used again to monitor the changes in the position and amplitude of the localized plasmon absorbance band (LSPR).

The outcome of this study is a better understanding of the formation of metallic nanoparticles thin films. The study of the effect of the film growth parameters are useful to control and tune the final properties of the sensing film. The presented sensing devices could then be further developed for environmental or industrial monitoring of solution containing organic compound.