Abstract

My Ph.D. thesis consists of experimental investigations in the following two areas.

(i) Stabilization of single soap bubbles and their spectroscopic investigation.
Observation of Marangoni effect driven upwardly mobile fluid layer in a soap bubble film.
Control of the fluid movement by controlling surfactant concentration gradient.

(ii) Synthesis of Au-nanoparticles (NPs) from reduction of $HAuCl_4$ by H_2O_2.
Generation of shape-selected Au-NPs.
Preparation of Au NP-conducting polyaniline (PANI) composite.
Solubilization of the composite in aqueous starch solution.
Colloidal polyaniline and Au-NPs-PANI composite nanoparticle synthesis.

The thesis consists of five chapters.

Chapter 1

Introduction

This chapter contains an overview of studies related to soap films and bubbles, microfluidics on a soap bubble film, soap films as a biological membrane and control of directional fluidic movement on a soap bubble film. It also contains a brief review of importance of nanotechnology and conducting polymers from technological perspectives. In this section a brief summary of the works performed in this thesis have been presented and the scopes for future development have also been discussed.

Chapter 2

In this chapter we describe observation and control of Marangoni convection driven upward fluid flow in a soap bubble. This chapter has been divided into two sub-chapters, with each sub-chapter containing introduction, experimental section, results and discussion and conclusion.

Chapter 2.1

Simultaneous measurement of flowing fluid layer and film thickness in a soap bubble using a UV-visible spectrophotometer

Here we report the observation of Marangoni convection driven fluid flow in various soap bubble films using a UV-visible spectrophotometer. Our observation of simultaneous time-dependent measurement of the thickness of fluid layer and thickness of the bubble film, is based on the fact that partial reflection of a beam of light from the surfaces of a thin, semitransparent film causes interference in the light beam when the film thickness is of the order of a wavelength of light. When the wavelength of light is scanned with a soap bubble film being in a UV- visible spectrophotometer, a set of maxima and minima of absorbance occurring at different wavelengths is observed. The number of such maxima and minima and the separation between two maxima or minima depend on the thickness of the bubble film and thus can be used to monitor the film thickness.

Marangoni effect driven fluid flow also resulted in the appearance of absorption maxima and minima similar to those due to film thickness. However the wavelength separation between two maxima or minima due to Marangoni effect driven flowing fluid layer was much smaller than to those due to film thickness and the intensity of absorbance due to Marangoni effect was also much smaller than that due to film thickness interference. Thus we could simultaneously measure film thickness and the thickness of the fluid layer driven by Marangoni effect. It was observed that the fluid layer thickness remained nearly constant for both vertical and horizontal bubbles (i.e. bubbles with alignment geometry different with respect to the support on which they rest) even though the film thickness had changed with time. The observed values of fluid layer thickness were about 6.94 ± 0.15 mm for a vertical bubble and about 4.75 ± 0.09 mm for a horizontal bubble. However no interference maxima or minima due to Marangoni driven fluid flow was observed for a single vertical soap film. Our observations suggest that Marangoni effect driven upward fluid movement helps restore the thickness of the film at the beginning after the formation of the bubble. Simultaneous gravitational drainage of water and surfactants occur from the film that reduces the film thickness with time. After a certain period in the lifetime of the bubble film no upwardly mobile fluid could be observed while the film thickness gradually decreased to its final equilibrium value reported to be of the order of 5-10 nm.

Chapter 2.2

Visible Spectroscopic Observation of Controlled Fluid Flow up along a Soap Bubble Film from a Pool of Solution

We have also achieved control over the fluid movement against gravity from a solution below, up along a bubble film, guided by Marangoni effect. Our method is based on controlling the surfactant concentration gradient between the bubble film and the surfactant solution on to which the bubble floats. The fluid flow was monitored by time dependent changes in the visible absorption spectrum of Rhodamine B, a laser dye, as it moved up along the bubble film from the solution below. We observed that when the concentration of surfactants in the solution below was higher than that in the film, fluid flow up along the bubble film could be observed. However, when the concentration of surfactant in the solution was equal to or lower than in the film, fluid movement could not be observed.

A small difference in initial surfactant concentration with a value as low as 2%, between the bubble and the pool of solution on which the bubble floats, is enough to initiate upward fluid movement. We could observe the controlled upward fluid movement until the surfactant concentration gradient was 5%. Further increase in the surfactant concentration gradient lead to dramatic increase in the flow rate that could not be followed using the present setup. Based upon our experimental evidences we concluded that Marangoni effect driven fluid movement up along a bubble film can be influenced by controlling the concentration gradient between the parent solutions, one from which the bubble is made and the other one on which the bubble floats.

Chapter 3

In this chapter we discuss the development of novel methods for the generation of Au nanoparticles (Au NPs), Au NP-conducting polyaniline composite (Au NP-PANI) and colloidal PANI and Au NP-PANI composite particles. The chapter consists of three sub-chapters with each describing introduction, experimental section, results and discussion and conclusions.

Chapter 3.1

A Simple Method of Electroless Deposition of Au NPs on Two and Three - Dimensional Surfaces of Various Materials

In this chapter we have reported a new method for the generation of Au nanoparticles in aqueous medium using H_2O_2 as the reducing agent. It is well known that in alkaline medium H_2O_2 reduces $HAuCl_4$ to Au-bulk precipitate. However, we have found that Au NPs are formed when $HAuCl_4$ in aqueous solution (acidic pH) is treated with H_2O_2. Addition of H_2O_2 to $HAuCl_4$ solution with controlled concentration produces colloidal Au NPs with characteristic plasmon absorption band at 530 nm. Au NPs could also be prepared using the same method in presence of microwave radiation. Transmission electron microscopic measurements confirmed the formation of NPs with average particle size of 20 nm in diameter when synthesized in presence of sodium dodecyl sulfate (SDS) micelles as stabilizer.

We have also observed that the Au NPs synthesized using the present method could be deposited on unfunctionalized surfaces of various materials. Previously treated glass and quartz plates as well as polymer surfaces in form of over-head projector paper (OHP) were kept in contact with Au NPs that were prepared from $HAuCl_4$ using H_2O_2 in presence of microwave radiation. The deposited NPs were characterized using UV-visible spectroscopy, scanning electron microscopy and X-ray diffraction method. The time-dependent gradual depositions of NPs on surfaces were also monitored by UV-visible spectroscopy, X-ray diffraction and optical microscopy.

Chapter 3.2

Synthesis of Au nanoparticle-Conductive polyaniline composite using H_2O_2 as both reducing and oxidizing agent

The reduction of $HAuCl_4$ by H_2O_2 with the formation of the Au NPs lead us to develop a method for the formation of Au nanoparticle-conducting polyaniline composite in aqueous medium using H_2O_2 both for reduction of $HAuCl_4$ and oxidation of aniline (polymerization). The incorporation of Au-NPs inside the polymer moiety increased the electrical conductivity by two orders of magnitude than the polymer itself (typical values being 0.3 Scm^{-1} for the Au NP-conducting PANI composite and 2.4×10^{-3} Scm^{-1} for the conducting polyaniline only). The incorporation of Au-NPs inside the polymer matrix was confirmed by X-ray diffraction study. The method is important as it reduces the number of steps typically required in a set of sequential reactions leading to formation of a composite.

Chapter 3.3

Synthesis of nanometer size aqueous colloidal conducting polyaniline and Au-nanoparticle-polyaniline composite particles in aqueous medium

In this sub-chapter we have discussed the controlled polymerization leading to the formation of colloidal conducting PANI and Au NP-PANI composite particles in aqueous micellar media (SDS, 1.2 x 10^{-2}M) in the presence of H_2O_2. The control was achieved by the introduction of the monomer, aniline from the vapor phase. The formation of the PANI and the composite was confirmed by UV-visible, FTIR and XRD measurements. TEM studies revealed that PANI particles of nanometer diameters were formed. On the other hand, in case of Au NP-PANI composite, self-assembled aggregated particles were formed in the nanometer domain. Core shell structure with a layer of PANI on the Au NP surface was also observed from the TEM studies.

Chapter 4

In this chapter we describe the use of starch for shape selective synthesis of Au NPs and for reversible encapsulation of PANI as well as Au NP-PANI composite. This chapter is divided into two sub-chapters.

Chapter 4.1

Reversible encapsulation of conducting polyaniline and Au nanoparticle-conducting polyaniline composite in starch

The insolubility of conductive polyaniline (PANI) in water and most of the common organic solvents has limited its application potential. Several strategies, primarily involving modification of the PANI backbone, have been devised for making the conducting polymer water soluble and thus biocompatible. In this aspect, we have solubilized the conducting PANI as well as Au NP-PANI composite in aqueous medium by incorporating them inside starch, which is known to attain helical conformation in presence of small molecules like I_2, n-butanol and carbon nanotubes. Encapsulation inside starch moiety here has been achieved by dissolving PANI as well as Au-NPs-PANI composite in aqueous solutions of starch with the help of an ultrasonicator bath. The encapsulation has been found to be completely reversible and both PANI and the composite could be recovered by introducing molecular iodine in the aqueous starch solution of either of them. In addition, we have shown that PANI could liberate I_2 from starch–iodine complex while the polymer itself gets encapsulated inside starch. Further, hydrolyzing starch by an enzyme could also liberate PANI from starch-PANI composite. Transmission electron microscopic observations suggest that PANI and the composite were dispersed in starch solution in the form of particles of average diameters on the order of 10-20 nm.

Chapter 4.2

Starch Mediated Shape-Selective Synthesis of Au-NPs with Tunable Longitudinal Plasmon Resonance

A large number of chemical and photochemical methods have been developed for the shape selective synthesis of the metal NPs where the optical, electronic and magnetic properties of these NPs can be tuned by varying the one, two and three-dimensional shapes of the NPs. Although a large number of synthetic methods exist for the shape-selective synthesis of Ag NPs, the same is not true for Au NPs. We have used starch as the template for the synthesis of Au-NPs of various shapes using H_2O_2 as the reducing agent in aqueous medium in the presence of ultrasonic wave. We have observed that, while keeping the concentration of the starch and H_2O_2 constant, the increase in the concentration of the parent metal salt $HAuCl_4$ led to the formation of NPs, the shape of which changed from spherical to triangular to hexagonal. This shape changes resulted in the appearance followed by red shift of the longitudinal plasmon resonance band while the transverse plasmon band remained nearly the same at 530 nm. The shape of the NPs formed was confirmed by TEM. Further, introduction of a starch digestive enzyme diastage (fungal) with enzyme activity 1:2000, in the starch-Au NP solution resulted in the precipitation of enzyme coated Au NPs, which may find use in targeted delivery at a desired site.

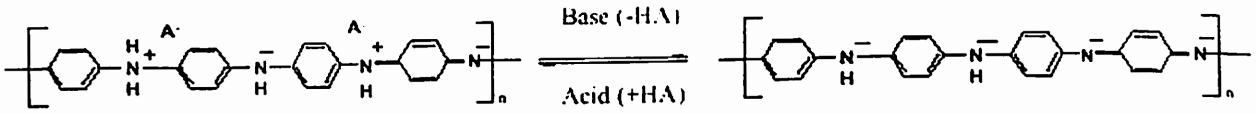
Chapter 5

In this chapter we describe a novel method for the deposition of polyaniline in a filter paper and use them for sensor applications.

Chapter 5.1

A polyaniline containing filter paper that can be used as a sensor, acid, base and end-point indicator and also filters acids and bases

Conducting form of PANI is a conjugated polymer with a number of unique properties. When cast into membranes, PANI shows unprecedented selectivity towards molecules essential for the development of sensors and actuators, membranes for gas separation as well as discrimination of chiral compounds in the presence of a chiral dopant. In this work, we have synthesized conducting form of PANI in a filter paper and then use the filter paper as (a) an acid, base and end-point indicator (b) as a sensor for the ammonia solution and vapor and (c) as a filter for acid and base. The use of the PANI containing filter paper as an acid-base sensor stems from the fact that emeraldine salt (green) and its base (blue) form can be reversibly converted in presence of a base and an acid respectively.



We have found that the PANI containing filter paper could detect the presence of ammonia in a solution with concentration as low as 14 ppm with the conversion of green filter paper into blue form. The ammonia vapor has also been detected in the same way by keeping the green paper above a solution with ammonia concentration as low as 45 ppm. Finally, the green filter paper could be used to decrease the pH of a basic solution and the blue paper could also be used to increase the pH of an acid solution by passing the appropriate solution through the relevant filter paper.