Chapter –II

Synthesis of Au Nanoparticles at "all" pH by H_2O_2 reduction of $HAuCl_4$

In this chapter, a new method for generation of Au NPs in the pH range of 2.9 through 11.2, by the reduction of $HAuCl_4$ using H_2O_2 as the reducing agent, would be reported. The study is based on an earlier observation from the laboratory that under acidic pH H_2O_2 could reduce $HAuCl_4$. This was further extended to obtain a general method of synthesis in a wider pH range. Although, at first thought the observations is against conventional wisdom of H_2O_2 being a poor reducing agent, they can be explained using standard electrochemical potentials involved with the reaction.

Chapter - III

A Water Soluble Polythiophene-Au Nanoparticle Composite for pH Sensing

In this chapter, development of a new pH sensor based on the fluorescence properties of polythiophene - Au NP composite prepared in water is to be reported. The composite was prepared by simultaneous reduction of $HAuCl_4$ to Au NPs and polymerization of thiophene in the medium in the presence of each other only. Electron spray ionization (ESI) – mass spectrum indicated that the composite mainly consisted of an polymer having a molecular mass of 783 amu. This means that the polymer consisted of six units of chlorothiophene and one thiophene monomer.

The polymer-nanoparticle composite, synthesized at pH 3.1 ± 0.05, when excited by light at 345 nm, exhibited a single intense emission peak with maximum at 435 nm. However, the maximum shifted gradualy to higher wavelengths with increase in pH of the solution, along with the appearance of small peak at lower wavelength. For example when the pH of the solution was increased to 6.0, the emission spectrum consisted of two peaks occurring at 390 nm and 465 nm. The results were explained by invoking the existence of two inter-convertible forms of polythiophene derivatives differing by the extent of protonation. At the lower pH values majority of the composite remained in protonated form (AH^+), having a characteristic single emission peak, while with increase in pH they were converted to a deprotonated form (A) giving rise to two emission peaks. At intermediate pH values, mixtures of the two species with concentrations corresponding to equilibria between the two forms existed. Also, the fluorescence measurements indicate that the two species were interconvertible and their concentrations could be changed by changing the pH of the medium.

Thus we have a new composite, where fluorescence of the polymer in the composite was used as a solution pH sensor.

Chapter – IV

Rapid and Sensitive Estimation of Bacteria by the Fluorescent Au Nanoparticle – Polythiophene Composite

The polythiophene-Au NP composite reported in the previous chapter was found to have its fluorescence sensitive to the presence of bacteria in aqueous solution and the change in fluorescence was maximum when the pH of the solution was kept at 3.0. For example, when the emission intensity of a 1:1 mixture of the aqueous solutions of the as-synthesized Au NP-polythiophene composite and various diluted bacterial cell suspensions were recorded, systematic decrease in the intensity was observed, with the increase in bacterial population. The decrease in fluorescence intensity of the composite with increasing bacterial concentration provided an excellent opportunity for quantitative estimation of the bacterial population. We have accounted for the decrease in emission intensity in terms of the effective concentration of the species AH^+ in the sample upon addition of bacterial cells. The relationship between the decrease in fluorescence intensity of the NP-polythiophene composite and bacterial cell concentration could be established from the well-known relationship between the intensity of fluorescence and the concentration of the fluorophore and which is can be written as follows.

$$Log\left(I_f^{C} - I_f^{Co}\right) = LogD + 2.3\varepsilon lx$$

where I_f^c is the intensity of steady-state fluorescence when the concentration of the fluorophore is c; x is a function of bacterial cell number and has the dimension of concentration. $D = Be^{-2.3\varepsilon lCo}$ and $B = \kappa F_{\lambda} I_0$

k is a proportionality constant; F_{λ} is the steady-state fluorescence intensity - at the emission maximum - per absorbed photon at the excitation wavelength; I_0 is the intensity of incident light, and ε is molar extinction coefficient at the excitation wavelength.

Interestingly, when the logarithm of difference in fluorescence intensities between that of the pure composite and that in the presence of different amount of bacteria was plotted against the logarithm of the number of bacterial cells a linear relationship was obtained. This was true for all four types of bacteria - *Pediococcus acidilactici* CFR K7, *Lactobacillus plantarum* MTCC 1325, *Escherichia coli* MTCC 433 and *Enterococcus faecalis* MTCC 439 - that were tested. The linear relationship being valid for all the four types of bacteria demonstrates the efficacy of the method in quantitative estimation of bacteria and the generality of the approach. Also important to mention here is that the lowest number of bacterial cells that can be estimated using the present scheme is 1000, indicating the sensitivity of the method. Remarkably, the present method allows estimation of logarithmic dilutions of bacterial cell numbers, which in the present case is on the order of 10^3-10^6 cells.

Chapter – V

Estimation of H_2O_2 using Fluorescence Emission of a Surfactant Stabilized Au Nanoparticle - Polythiophene Composite

Here we report the use of a new Au Nanoparticle- polythiophene composite in the rapid and quantitative detection of aqueous H_2O_2. The method is based on changes in the visible absorption of the Au NPs as well as fluorescence of the polythiophene in the composite, in the presence of various amount of H_2O_2. The composite was synthesized by reaction of thiophene with $HAuCl_4$ in the presence of a surfactant, sodium dodecyl sulfate (SDS).

We observed that the emission intensity of the composite decreased systematically with increase in the concentrations of H_2O_2 in the sample. In our case we studied the effect of H_2O_2, varying its concentration range from 10 mM to 0.2 mM. A plot of the area under the fluorescence curves versus the concentration of H_2O_2 indicated a linear dependence of emission on the concentration of the peroxide. It was observed that the linearity was followed when the concentrations of the H_2O_2 in the medium was below 4 mM. At concentrations above 4 mM the dependence varied randomly and is thus not reported. It's noteworthy to mention that the lowest concentration of H_2O_2 that could be measured using the change in fluorescence was 0.23 mM. This value is similar to literature values of the limits of detection of H_2O_2 using the conventional methods. The decrease in fluorescence intensity of the composite with increasing H_2O_2 concentration provides an excellent opportunity for quantitative and rather accurate estimation of the H_2O_2 concentration.

Chapter – VI

Electrochemical Actuation of Growing Copper Dendrimers in Water

This chapter reports the observation of electrochemical actuation in growing dendritic fibers made of self-assembled Cu nanostructures (of 100 nm or less in diameter) or its composite with Au NPs, on the metallic cathode of an ordinary aqueous electrochemical cell. This could be achieved when a Cu anode and another metal cathode was placed in aqueous solution of either dilute HCl or $CuSO_4$, or $CuCl_2$, or H_2O, and upon application of a D.C. voltage at 1.5-12.0 V. The actuation could be observed with an on-off cycle of the applied voltage in the above range. The phenomenon was also observed with the growth of bimetallic structures using a number of electrolytes such as $Ag(NO_3)$, $Pb(NO_3)_2$, $CoCl_2$, $NiCl_2$, $CdCl_2$, $ZnCl_2$, and $HAuCl_4$. The fibrous structures remained stretched as they grew longer with time in the presence of an applied voltage. The extent of actuation was dependent on the applied voltage, the concentration of Cu^{2+} ions in the solution, and also on ions such as Na^+, which did not get deposited at the cathode. The observed phenomena under different conditions were explained using the principles of electrocapillarity.