Chapter 7

Summary and Prospects for Future Works

In this chapter we summarize the work presented in the thesis, highlight the significant results and also indicate the importance and possible future prospects. In broad terms the work presented in the thesis can be classified as follows:

1. Formation and characterization of different types of ultrathin films on gold substrate for example, Langmuir-Blodgett (LB) film, self-assembled monolayer (SAM) and polyelectrolytes layer-by-layer assembly (LbL).

2. Formation and characterization of diverse range of nanostructures in bulk and in the form of a thin film, from a porphyrin derivative and polyaniline (PANI): Optical properties and electrochemical lead sensing.

3. A simple route for electrochemically synthesizing the nanocomposite film of palladium and polyethylenedioxythiophene (PEDOT). The electrocatalytic studies on the nanocomposite film towards ethanol oxidation in alkaline medium and hydrogen evolution reaction (HER) in acidic medium.

4. Electrochemical synthesis and characterization of the nanocomposite film of palladium and polyaniline (PANI). The electrocatalytic studies on the nanocomposite film towards the oxidation of small chain alcohols (ethanol and methanol) in alkaline medium and formic acid oxidation in acidic medium.

5. Electrochemical synthesis and characterization of nanocomposite films of gold with different conducting polymers namely; polyaniline (PANI), polypyrrole (PPY), polythiophene (PTP) and polyethylenedioxythiophene (PEDOT). The electrocatalytic studies on nanocomposite films towards ethanol oxidation in alkaline medium.
(1) Formation and characterization of different types of ultrathin films on gold electrode: Langmuir-Blodgett (LB) film, self-assembled monolayer (SAM) and polyelectrolyte layer-by-layer assembly (LbL)

In this work, we have prepared and characterized different types of ultrathin molecular films on gold substrate. We have also studied the electrochemical properties of these films in aqueous and nonaqueous systems. The electron transfer and ion permeation studies were carried out through the cholesterol monolayers and multilayer films formed on self-assembled monolayers of thiophenol (TP) and 2-naphthalenethiol (2NT) on Au substrate. The molecular films of cholesterol have also been characterized using STM, AFM and grazing angle FTIR studies. We observed that the charge transfer resistance and interfacial capacitance values depend upon the structure of the monolayer. A model is proposed for the structure of the cholesterol molecules on 2NT SAM modified surface.

In the second part of the work, the electrochemical barrier properties of the LB films of a discotic liquid crystal (hexaalkoxytriphenylene with bromide counterion (PyTp) and its complex with DNA were studied with two different redox probes namely, potassium ferrocyanide/ferricyanide and ferrocene. The study shows that in the case of ferrocene redox system the bridge-mediated electron transfer process is responsible for the very low charge transfer resistance values. However, the high charge transfer resistance values obtained in the case of potassium ferrocyanide system is due to the fact that the LB film of DNA-discogen is impermeable to the ferrocyanide ions.

In the third part, we have analyzed the self-assembly of the inclusion complexes formed between β-cyclodextrin and thiocholesterol. Electrochemical and AFM studies were carried out for the characterization of the SAM. The self-assembled monolayer was imaged by using lateral force microscopy (LFM) and the force-distance measurements between the hydrophilic AFM tip and the sample were also carried out. Two distinct regions were found in each of the cases having hydrophilic and hydrophobic nature. Friction images were analyzed to understand the dissimilar chemical nature of both the regions. Hydrophilic region was made up of cyclodextrin inclusion complex whereas the hydrophobic region was composed of only thiocholesterol molecules. Force-distance spectroscopy reveals the greater tip-surface interaction in hydrophilic regions than the hydrophobic regions. Electrochemical studies such as cyclic voltammetry and usual dye aggregates.
electrochemical impedance spectroscopy were also carried out in aqueous medium to obtain the further insight to the inclusion complex SAM.

The final part of the chapter deals with the layer-by-layer (LbL) films of oppositely charged polyelectrolytes namely, polystyrenesulfonate (PSS) and polyallylamine hydrochloride (PAH). We have analyzed the polyelectrolyte films with the help of AFM and cyclic voltammetry. The studies show an increase in the roughness and electron transfer barrier properties (in potassium ferrocyanide/ferricyanide system) with the increasing thickness of the film.

(2) Formation and characterization of nanostructures of a porphyrin derivative and polyaniline (PANI): Optical properties and electrochemical lead sensing

We have studied the nanoparticles formed by a porphyrin derivative 4,4',4″,4‴-(porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid) (PTBA) and polyaniline (PANI) in a DMF/water mixture. The nanostructures were characterized with the help of AFM by drop casting them onto a freshly cleaved mica sheet. Nonlinear optical absorption measurements were carried out at 532 nm, which show that the nanocomposite has an enhanced optical limiting property compared to the precursor compounds PTBA and PANI.

We have also presented a simple technique to form nanostructures by layer-by-layer assembly. These nanostructures are composed of alternate PTBA-PANI layers and grow perpendicular to the surface. The morphological analysis of the LbL films was carried out using an AFM in tapping mode. Multilayer films of 4 and 8 layers were formed on gold-coated mica. The modified electrode was used for lead detection and it was observed that it is capable of detecting lead down to 100 ppb with the help of anodic stripping voltammetry.

We have also prepared PTBA nanofibers, which are essentially the J-aggregates of porphyrin. The nanofibers were characterized with the help of AFM, UV-vis spectroscopy and PL spectra. It was observed that the nanofibers are highly emissive, contrary to the behavior of usual dye aggregates.
(3) A novel electrochemical synthesis of nanocomposite film of palladium and polyethylenedioxythiophene (PEDOT) and its electrocatalytic studies

We have proposed a novel single step electrochemical method of synthesizing Pd-PEDOT nanocomposite film on gold surface by the galvanostatic dissolution of Pd wires in the acidic EDOT solution. A thin film of nanocomposite containing Pd nanoparticles embedded in the polymer matrix was formed on the surface. The nanocomposite film surface was characterized by using SEM, EDAX, ICP-MS, AFM and electrochemical experiments. The ICP-MS and Pd oxides stripping peak in cyclic voltammetry show that the Pd loading in the nanocomposite is quite low. Nevertheless, the nanocomposite film exhibited good stability over time and proved to be an effective electrocatalyst for hydrogen evolution and ethanol electro-oxidation reactions in these experiments. The activation energy calculations and Tafel plot analysis at different temperatures further confirm the excellent catalytic activity of the nanocomposite film on gold surface.

(4) Electrochemical synthesis and characterization of the nanocomposite film of palladium and polyaniline (PANI) and its electrocatalytic studies

In this work, we have described a novel electrochemical route to deposit Pd-PANI nanofiber film on electrode surface. We have demonstrated that the galvanostatic dissolution of Pd wire in the acidic aniline solution yields Pd-PANI nanofiber film on the cathode surface. The film was characterized using SEM, EDAX, AFM, XRD and XPS. The SEM images of the surface show the nanofibers of Pd-PANI nanocomposite with Pd nanoparticles adhering on the PANI surface.

The Pd-PANI nanofiber film on the electrode shows a different voltammetric behavior from that of the pure Pd wire electrode for hydrogen adsorption and absorption in acidic medium. The excellent electrocatalytic activity of the nanofiber film electrode was confirmed from the electro-oxidation of formic acid in acidic medium and alcohols (ethanol and methanol) in alkaline medium. The activation energy calculations and Tafel plot analysis at different temperatures were also carried out to understand the kinetics of the electrocatalysis on Pd-PANI modified surface. These studies show that the nanofiber film of Pd-PANI is a potential substitute of Pt in direct fuel cells (DFCs). The mass current densities observed in all the experiments were either superior or comparable to the best available electro-oxidation currents in the literature.
(5) Electrochemical synthesis and characterization of nanocomposite films of gold with different conducting polymers and their electrocatalytic studies

In this work a single step electrochemical method to prepare nanocomposite films of gold and different conducting polymers namely; polyaniline (PANI), polypyrrole (PPY), polythiophene (PTP) and polyethylenedioxythiophene (PEDOT) in ambient conditions is proposed. The nanocomposite films were characterized using SEM, EDAX, FTIR spectroscopy and AFM.

The nanocomposite films were found to be very efficient catalysts for ethanol electro-oxidation reaction. The activation energy calculations and Tafel plot analysis at different temperatures were carried out in order to study the kinetics of the electro-oxidation. Based on the electrocatalysis experimental results, we conclude that Au-PANI nanocomposite is the best electrocatalytic material among all the Au-CP nanocomposites studied in this work in terms of the low activation energy, high electro-oxidation current and low onset potential required for the ethanol electro-oxidation reaction.

Prospects for future works

The work presented in the thesis can be broadly divided into two parts with the first part dealing with the formation of thin films of different materials and their applications. The second part deals with the electrocatalysis studies with metal and conducting polymers nanocomposites. We summarize below the importance of these studies and the prospects and scope for future work.

(1) In chapter 3 and 4 we have given an account of different types of ultrathin films that can be formed on different substrates i.e. the Langmuir-Blodgett (LB), self-assembled monolayer (SAM) and layer-by-layer (LbL) films. Among them, the layer-by-layer assembly has several potential applications in biosensor devices due to its ability to accommodate bio-molecules in its soft surroundings.

(2) We have carried out the immobilization of cholesterol on different self-assembled monolayers modified surfaces, which is important from the point of view of biological systems. For example the immobilization of certain phospholipids along with cholesterol on gold surface can mimic the bilayer membrane on solid surfaces. The electron transfer and ionic mobility studies through these model membranes can have considerable significance in biology.
(3) Nanoscale films produced with the above techniques find applications in the fabrication of nanomaterials and molecular electronics. Fundamental processes such as charge transfer mechanisms involving biomolecules can also be investigated at the molecular level. For example, the study of the DNA complex films will be helpful in understanding the nature of electrical and ion conduction mechanism of these biomolecular films and in designing the anisotropic ion conducting materials for different applications.

(4) Our studies with cyclodextrins and thiocholesterol inclusion complex SAMs are the examples of how patterned hydrophilic and hydrophobic surfaces can be prepared. The mixed hydrophilic and hydrophobic surfaces of this type will be useful in molecular recognition, pathogen detection and bio-sensing applications in general.

(5) In fourth chapter we have discussed the synthesis of nanostructures from a porphyrin derivative and polyaniline and their LbL film. The present study is a clear demonstration of the fact that under favorable conditions for nanoparticle formation, even a simple procedure like mixing of two media can lead to a substantial modification of the net nonlinear optical property of a given chemical system. Different conducting polymers can also be used for the preparation of the nanostructures, which have interesting optical properties. In addition, the electrochemical method of sensing lead shows the potential of the nanostructured thin film in metal ion sensing.

(6) The nanofibers, which are essentially the J-aggregates of porphyrin show enhanced emission property. The interesting results obtained from the optical and electrochemical studies signify the importance of these nanostructures in various optical and sensing devices.

(7) Our studies with Pd-PEDOT and Pd-PANI nanocomposite films have shown that these films can find potential applications in direct fuel cells (DFCs). Most of the electrocatalytic materials utilized for fuel cells are either metals or more specifically the noble metals. Some of the main catalytic materials include platinum, iridium, ruthenium, palladium, gold and silver. As of now the most common electrocatalytic material is platinum metal because of its ability to function close to the thermodynamic potential. However the high price of Pt has led researchers to work on developing alternative catalytic materials. A few of the non-noble metals have also demonstrated catalytic activity, often in combination with the noble elements, and they include nickel, iron, cobalt, chromium, vanadium, molybdenum, tin, tungsten. The study shows that a
similar method when adopted for non-noble metals in combinations with conducting polymers will lead to interesting possibilities in electrocatalysis.

(8) We believe that further studies will reveal that the mesoporous Pd-PEDOT nanocomposite and Pd-PANI nanofiber films prepared by the method described in this work may find wide applications as materials for catalysts, sensors and hydrogen storage.

(9) We have formed gold and conducting polymers nanocomposites, which may find useful applications in electrocatalysis. A detailed study, which includes the study of the electrocatalysis kinetics, Tafel slope analysis and activation energy calculation, carried out by us reveals the importance of these nanocomposite films in ethanol electrocatalysis in alkaline medium. Further studies will throw more light on the practical applications of these materials in alkaline fuel cells.

(10) The work presented here on metal-conducting polymer nanocomposites primarily focuses on the method of preparation and nature of these films. The possible potential applications have been explored and discussed. However, to confirm their utility in practical device applications, for example in fuel cells, a more detailed study of the material stability at higher temperatures, integrity in strong acidic and alkaline environments and the effect of surface contaminations by adsorbed impurities on the catalytic activity etc., are required.