SYNOPSIS

Electrochemical studies and molecular self-assembly on surfaces in surfactant based systems

This thesis deals with the self-aggregated structures of surfactants such as micelles, microemulsion and lyotropic liquid crystalline phases as electrolytic systems to study the electrochemical reactions and the molecular self-assembly on metallic surfaces. More specifically, this work concerns with exploring the surfactant stabilized systems in understanding the fundamental aspects of electron transfer kinetics through organic molecular monolayer films and in applications of such systems in technologically important areas with specific examples of liquid crystal template deposition and supercapacitors. As model systems, we have examined the utility of a non-ionic surfactant, Triton X-100 in binary system of Triton X-100-water and ternary system of Triton X-100-water and a polyelectrolyte in electrochemical studies. The distinct order within the electrolyte influences the electron transfer behaviour of redox species exhibiting the microelectrode array characteristics.

A study of molecular self-assembly on gold surface using the hexagonal lyotropic liquid crystalline phase as a solvating medium has been proposed in this work. This method has several distinct advantages over the traditional methods of using organic solvents. The ability to produce monolayers that are structurally ordered, well oriented, compact and having ultra low defect density has been demonstrated. A detailed investigation of the long chain aliphatic thiols, aromatic thiols and alkoxycyanobiphenyl thiols having different chain lengths of C₅, C₈ and C₁₀ prepared using this method was undertaken using two different redox probes to evaluate the blocking ability of
these ultra thin films. The electron transfer processes represented by these two redox species concern the inner sphere and outer sphere mechanisms. These studies have implications in understanding the electron transfer kinetics in some biological systems also.

More specifically, we have carried out template electrodeposition, study of electron transfer reactions of redox probe molecules and self-assembled monolayers of thiol compounds on gold surface using several self-aggregated structures of surfactants. We have highlighted the potential utility of the materials prepared using template electrodeposition in supercapacitor applications and as a hydrogen-evolving cathode in electrocatalysis. In our investigations, we have extensively used electrochemical techniques such as cyclic voltammetry, electrochemical impedance spectroscopy and gold oxide stripping analysis, surface analytical techniques namely grazing angle FTIR spectroscopy and X-ray diffraction (XRD) and microscopic techniques such as scanning electron microscopy (SEM) and scanning tunneling microscopy (STM) essentially to characterize the materials and to study different processes occurring at the electrode | electrolyte interface.

We have chosen a few self-aggregated structures of surfactants as an electrolytic medium in our studies due to their potential ability to mimic the biological systems and to understand the various electron transfer processes occurring in the biological systems. These systems exhibit very low conductivity that makes the study of several processes occurring at the interface, an interesting one. We find from literature that there are a very few studies on electrochemistry and molecular self-assembly on surfaces based on surfactant stabilized electrolytic systems. In what follows, we have briefly described some of the significant results and conclusions derived from our experimental work.
Chapter 1: Introduction

In this chapter, we have described the importance of our studies and aims and scope of our research investigation. This chapter has been divided into three parts. The first part deals with an introduction to surfactant, the chemistry and structure of surfactant, the different self-aggregated structures such as micelles, reverse micelles, microemulsion phase and several liquid crystalline phases along with a general phase diagram of a ternary system consisting of water, oil and surfactant components. Surfactants, a common name derived from surface-active agents, are amphiphilic molecules containing two parts in their structure namely, the hydrophilic head group and the hydrophobic tail group. The essential function of these surfactant molecules is to reduce the surface tension at the interface or at the surface and to allow easier spreading of molecules. Above a concentration called critical micellar concentration (CMC) at which the micelle formation begins, these surfactant molecules self-aggregated themselves to form a variety of structures namely micelles, reverse micelles, microemulsion phase and liquid crystalline phases. These self-aggregated structures in aqueous solution can be transformed from one phase to another phase by changing the solution conditions namely the electrolyte and pH of the medium. There are two important factors viz., the thermodynamics of self-assembly and the forces operating between these molecules within the aggregates play a vital role in determining the formation of self-assembled structures. A general phase diagram of a ternary system consisting of water, oil and surfactant obtained using Winsor’s classification explains a variety of possible self-aggregated structures that can be produced using this system.

The second part deals with a brief introduction to the field of self-assembled monolayer (SAM). The nature of bonding involved in SAM and the
structure of the monolayer have also been explained. Self-assembled monolayers are molecular assemblies on metallic or non-metallic surfaces that are formed spontaneously by immersion of an appropriate substrate into a solution containing thiol compounds, leading to the formation of a highly ordered, well-packed, oriented, compact, dense monolayer with very low defect density. There are two methods of self-assembly namely Langmuir-Blodgett method and self-assembled monolayer that can yield organic monolayers on surfaces. In our research work, we have used self-assembled monolayer method for the preparation and characterization of monolayers of aliphatic thiols, aromatic thiols and alkoxy cyanobiphenyl thiols on gold surface. In this section, after describing the method of preparation of SAMs, various techniques that have been used to characterize the monolayers and their structure on gold surface are presented and briefly explained. These techniques include contact angle measurement, ellipsometry, surface plasmon resonance (SPR) spectroscopy, Infrared and Raman spectroscopy, Quartz crystal microbalance (QCM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (HREELS), low energy electron diffraction (LEED), scanning tunneling and atomic force microscopy and electrochemical techniques. Based on these techniques, it is found that the thiol molecules posses a high degree of order and stability and these monolayers form a (3\sqrt{3}\times3) R 30^0 overlayer structure with the underlying Au(111) substrate. The alkyl chains of the monolayer are tilted by approximately 30^0 from the surface in order to maximize the van der Waals interactions. Since the SAMs of thiols can be formed on metal surfaces namely Au, Ag and Pt, the same metal electrodes coated with the monolayer can be used as the working electrodes and the SAMs can be characterized using electrochemical techniques such as cyclic voltammetry, electrochemical
impedance spectroscopy, gold oxide stripping analysis and capacitance measurements. A measure of degree of packing of the SAMs on the gold surface can be obtained by comparing their dielectric constant determined from the electrode capacitance. The distribution of pinholes and defects within the monolayer can be understood based on pinholes and defects analysis using their impedance data. The third and final part of this chapter contains the aims and scope of our present research work.

Chapter 2: Experimental Section

This chapter describes the details of method of preparation of electrodes, electrode pre-treatment procedures and electrochemical cell arrangements of our experimental setup that has been used to carry out the research investigation. The electrochemical cell, which has been designed and fabricated in our laboratory, is described in this chapter that is followed by different procedures employed for the preparation of working electrodes. A detailed description of various experimental techniques used in our research work is provided. The experimental work involves mainly a variety of electrochemical techniques such as cyclic voltammetry, electrochemical impedance spectroscopy, gold oxide stripping analysis, chronoamperometry, chronopotentiometry and Tafel plot analysis. Apart from this, we have also carried out surface analytical techniques namely X-ray diffraction (XRD) and grazing angle FTIR spectroscopy and microscopic techniques such as scanning electron microscopy (SEM), scanning tunneling microscopy (STM) and polarizing light microscopy (PLM) in our studies. The working principle and the importance of these techniques are also briefly discussed.
In this chapter, we have discussed the method of template electrodeposition of nickel and also the studies of electron transfer reactions of redox probe molecules using some surfactants self-aggregated systems as electrolytic media. We have used a binary system consisting of water and Triton X-100 and a ternary system consisting of water, Triton X-100 and poly(acrylic acid) components exhibiting a hexagonal liquid crystalline phase and a ternary mixture containing water, Triton X-100 and toluene compositions showing microemulsion phase as templates for electrodeposition of nickel and electrolytic media for electron transfer studies. We find that the process of mass transfer plays a vital role in the determination of surface morphology and electrochemical properties of template deposited materials. The role of mass transfer and its effect on the surface topography of the electrodeposited nickel has also been studied under the applied magnetic field of 1 Teslas. The surface morphology of the template deposited nickel material was characterized using SEM, STM and XRD. The electrochemical properties and surface area determination were carried out using electrochemical techniques. This chapter has been divided into four sections. The first section deals with the template electrodeposition of nickel using a new hexagonal liquid crystalline phase as a template. In this section, we have described a new method of fabricating the high surface area materials. We have prepared a high surface area nickel material with the roughness factor of 3620, the highest value reported for any electrodeposited nickel in literature corresponding to a specific surface area of 650 cm$^2$ with a double layer capacitance of 338 mF/cm$^2$ using the template
electrodeposition. We have shown that the high surface area essentially arises from the flooded pear shaped porous structure and densely distributed nickel nanoparticles within as well as in between the pores. SEM, STM and XRD studies proved the porous structure of the nickel material and the existence of individual nickel nanoparticle. Cyclic voltammetry and electrochemical impedance spectroscopy were used to determine the surface area of the porous nickel electrodes and the current-potential characteristics of hydrogen evolution reaction (her) on the nickel electrode was determined using chronoamperometry.

The second section deals with the study on the effect of applied magnetic field on the electrodeposition of nickel. A magnetic field of 1Tesla was applied during the electrolysis of nickel at an angle of 45° to the cathodic nickel surface. The surface topography of nickel was characterized using SEM, STM and size of the nickel nanoparticles was determined using XRD. In contrast to a layer type growth observed in the absence of magnetic field, a domain growth with nickel nanoparticles mainly concentrated at domain boundaries was observed in the presence of an applied magnetic field of 1Tesla during the electrodeposition of nickel. We find a large lowering of overpotential during the magnetoelectrolysis of nickel and it is attributed to an increase in the rate of metal deposition brought about by enhanced mass transfer induced by applied magnetic field. We have also observed a negative shift in the rest potential due to the change in chemical potential of the ferromagnetic nickel that has been brought about by the domain movements and consequent shift in Fermi energy levels due to the application of external magnetic field.

Third section of this chapter contains the discussion on template electrodeposition of nickel using a microemulsion phase, as mentioned above, as a template. The surface morphology of the template deposited nickel material
was characterized using SEM and the surface area was determined using cyclic voltammetry. In this case, we have obtained a fractal growth of nickel surface having the particles of size ranging from 1μm to 2μm and there is no porous structure formation.

The fourth and final part of this chapter contains the electron transfer studies of redox probe molecules using surfactant self-aggregated systems as electrolytic media. We have used micelles formed from sodium dodecyl sulphate (SDS), a microemulsion phase consisting of water, Triton X-100 and p-Xylene/toluene compositions, a hexagonal liquid crystalline phase and a lamellar phase consisting of a ternary mixture of water, Triton X-100 and decanol compositions as electrolytic media for electron transfer studies. We find from the cyclic voltammetry and electrochemical impedance spectroscopic studies that the electron transfer reaction of ruthenium complex is under charge transfer control in presence of a micellar medium. We have studied the electron transfer reaction of [Fe(CN)₆]³⁻⁴⁺ redox couple in the microemulsion phase using cyclic voltammetry and impedance spectroscopy. In contrast to the diffusion controlled process arises from the semi infinite linear diffusion of the redox species observed in normal aqueous electrolytic medium, the microemulsion phase exhibit the characteristics of microelectrode array behaviour for the redox reaction due to the radial diffusion of species in the aqueous micro domains formed by the surfactant molecules. We have also studied the electron transfer reaction in the hexagonal liquid crystalline phase and found that the redox reaction is reversible indicating that the process is fully diffusion controlled.
Chapter 4: Electrochemical studies on self-assembled monolayers of some aromatic thiols and alkoxy cyanobiphenyl thiols on gold surface

This chapter deals with our studies on self-assembled monolayers of some aromatic thiols and alkoxy cyanobiphenyl thiols on gold surface. We have studied and characterized the monolayer formation of 2-naphthalenethiol (NT), thiophenol (TP), o-aminothiophenol (o-ATP), p-aminothiophenol (p-ATP) and alkoxy cyanobiphenyl thiols having different chain lengths of C5, C8 and C10 on gold surface using organic solvents as an adsorbing medium. The structural arrangement and orientation of some of these monolayers were characterized by grazing angle FTIR spectroscopy and scanning tunneling microscopy. The barrier properties and insulating properties of these monolayers were evaluated by studying the electron transfer reactions of redox probe molecules on the SAM modified surface using cyclic voltammetry and electrochemical impedance spectroscopy. The surface coverage (θ) and charge transfer resistance (Rct) values, which is a measure of the blocking ability of the monolayers, were determined from their impedance data. In addition impedance data were also used to determine the distribution of pinholes and defects within the monolayer using the pinholes and defect analysis. From our experimental work and results, we find that the self-assembled monolayers of these aromatic thiols form a stable, reproducible but poorly blocking monolayer on Au surface. We have tried to improve their blocking ability towards the redox reactions using a variety of methods such as potential cycling, annealing and mixed SAM formation. From CV and EIS studies, we find that although the redox reaction of potassium ferrocyanide complex is inhibited, ruthenium redox reaction is not significantly inhibited in all these cases of SAMs of aromatic thiols on Au surface. Based on the results, we have proposed that the electron transfer
reaction of ruthenium redox couple takes place by a tunneling mechanism through the high π-electron density aromatic ring acting as a bridge between the SAM modified electrodes and ruthenium complex. In all these cases of aromatic SAMs, we have obtained a surface coverage value of >99.9% for the monolayer on Au surface.

This chapter has been divided into three parts. The first part deals with the formation and characterization of self-assembled monolayer of 2-naphthalenethiol on Au surface that has been studied and reported for the first time in literature. Based on STM and FTIR studies, we have proposed a new structure of $\sqrt{3} \times 3 R \ 30^\circ$ overlayer structure for the SAM of 2-naphthalenethiol on Au surface. We have also studied the kinetics of monolayer formation in this case, and found that the self-assembly follows Langmuir adsorption isotherm. From the results of cyclic voltammetry and impedance measurements using redox probes we have shown that 2-naphthalenethiol on Au forms a stable, reproducible but moderately blocking monolayer. We also find that annealing of the SAM modified surface at $720^\circ \pm 20^\circ$C remarkably improves the blocking property of the monolayer of 2-naphthalenethiol on Au surface.

The second part deals with the studies on the structural integrity and barrier properties of self-assembled monolayers of TP, o-ATP and p-ATP on polycrystalline Au surface using electrochemical techniques. We have also studied the effect of pH on the blocking ability of the SAMs of aminothiophenols on Au surface. The results of cyclic voltammetry and impedance spectroscopy measurements show that these aromatic thiols form stable and reproducible but moderately blocking monolayers. We have tried to improve the blocking ability of these monolayers by potential cycling and mixed SAM formation with 1-Octanethiol and 1,6-Hexanedicthiol. From the results of cyclic voltammetry and impedance spectroscopic studies, we have
shown that the blocking ability of these monolayers is significantly improved by potential cycling and by mixed SAM formation.

The third and final part of this chapter contains the studies on self-assembled monolayers of liquid crystalline thiol-terminated alkoxy cyanobiphenyl molecules having different alkyl chain lengths of C₅, C₈ and C₁₀ on Au surface for the first time using electrochemical techniques. A combined aromatic-aliphatic system of alkoxy cyanobiphenyl thiols exhibits some interesting electron transfer characteristics. We find that these alkoxy cyanobiphenyl thiol molecules mediate electron transfer between the Au electrode and [Ru(NH₃)₆]²⁺/³⁺ redox couple when the alkyl chain length is shorter (C₅) and inhibit the process when the alkyl chain length is longer (C₈ & C₁₀). We also find that the rate constant values of [Fe(CN)₆]³⁻/⁴⁻ redox couple are decreased by almost four orders of magnitude for the SAM modified electrodes when compared to the bare Au electrode.

**Chapter 5: Study on the barrier properties and interfacial properties of self-assembled monolayers (SAMs) of aliphatic, aromatic and alkoxy cyanobiphenyl thiols on gold surface prepared using a lyotropic liquid crystalline phase as an adsorbing medium**

In this chapter, we have described a new method of preparing self-assembled monolayers of thiols on gold surface using a hexagonal liquid crystalline phase consisting of water and Triton X-100 as an adsorbing medium. For monolayer preparation, the corresponding thiol was added to the hexagonal liquid crystalline phase and used as an adsorbing medium. The triphase system containing in addition to water/Triton X-100, the corresponding thiol molecules showed the hexagonal lyotropic liquid crystalline phase behaviour that has been
characterized using polarizing light microscopy (PLM) and X-ray diffraction (XRD) studies. We have studied and characterized the monolayer formation of some aliphatic thiols, aromatic thiols and alkoxy cyanobiphenyl thiols on gold surface using the above-mentioned hexagonal liquid crystalline phase as an adsorbing medium. We have used aliphatic thiols namely decanethiol and hexadecanethiol, aromatic thiols such as 2-naphthalenethiol, thiophenol and p-aminothiophenol and alkoxy cyanobiphenyl thiols having different chain lengths of C₅, C₈ and C₁₀ for monolayer formation on Au surface. The barrier properties and interfacial properties of these monolayers on Au surface were evaluated using electrochemical techniques and spectroscopic techniques. We have compared our results and the blocking ability of the monolayers prepared using the hexagonal liquid crystalline phase with that of the corresponding monolayer formed using the organic solvents such as ethanol and dichloromethane as an adsorbing medium. The surface coverage (θ) and charge transfer resistance (Rₑₓ) values, which is a measure of the electrochemical blocking ability of the monolayers, were determined from their impedance data. In addition, the impedance data were also used to determine the distribution of pinholes and defects within the monolayer using the pinholes and defect analysis. From our experimental results, we find that the SAMs formed from the hexagonal liquid crystalline phase are highly compact and have excellent electrochemical blocking ability towards the redox probes than the SAMs prepared from commonly used organic solvents such as ethanol and dichloromethane (conventional methods) in the cases of aliphatic and alkoxy cyanobiphenyl thiols on Au surface. We believe that the hexagonal liquid crystalline phase provides a highly hydrophobic environment to solubilize the thiol molecules and later to facilitate their delivery to the gold surface to form the monolayer. The use of aqueous medium provides a route for the formation of a highly compact, dense
monolayer with almost defect free structure, which is crucial in the applications and commercial development of devices based on SAM and also eliminates several major problems associated with the organic solvents used for the preparation of monolayer. Based on the results, we have also proposed a possible mechanism for the monolayer formation using the hexagonal liquid crystalline phase as an adsorbing medium.

This chapter has been divided into three parts. The first part deals with the preparation and characterization of self-assembled monolayers of aliphatic thiols namely decanethiol and hexadecanethiol on Au surface using the hexagonal liquid crystalline phase as an adsorbing medium. The structure and orientation of the monolayers were characterized by grazing angle FTIR spectroscopy. We have ruled out the multilayer formation and co-adsorption of surfactant molecules on Au surface using grazing angle FTIR spectroscopy and capacitance measurements. The second and third parts of this chapter contain the study of monolayer formation using aromatic thiols and alkoxycyanobiphenyl thiols of different chain lengths on gold surface using the above-mentioned hexagonal liquid crystalline phase as an adsorbing medium. We find from our experimental results that in the case of SAM of aromatic thiols on Au surface, the monolayer formed from organic solvents exhibits a better blocking property and insulating property than the corresponding SAM obtained using the hexagonal liquid crystalline phase. This may be due to the entrapment of small aromatic thiols in the liquid crystalline phase due to some interactions between the thiol molecules and the surfactant, which prevent the delivery of these aromatic thiol molecules to the gold surface. We also find that the rate constants of $[\text{Fe(CN)}_6]^{3-\text{+}}$ and $[\text{Ru(NH}_3)_6]^{2+\text{+}}$ redox couples are very much lower in the case of monolayers of aliphatic and alkoxycyanobiphenyl thiols prepared in liquid crystalline phase when compared to the SAM formed
in 1mM thiol in ethanol and dichloromethane solvents respectively, suggesting a better electrochemical blocking ability of the SAMs in the former case. Our results suggest that the SAMs of very low defect density and extremely low ionic permeability can be prepared when a hexagonal lyotropic liquid crystalline phase is used as an adsorbing medium. In all these cases of SAMs prepared from the hexagonal liquid crystalline phase, we have obtained a surface coverage value of >99.99% for the monolayer on Au surface.

**Chapter 6: Applications of high surface area porous nickel as a supercapacitor electrode material and as a hydrogen evolution catalyst**

In this chapter, we have shown that the high surface area porous nickel prepared using the template electrodeposition has potential applications as supercapacitor electrode material and as a hydrogen-evolving cathode in electrocatalysis.

This chapter has been divided into two parts. The first part deals with the experiments performed to evaluate the high surface area porous nickel as an electrode material in supercapacitor applications. We have evaluated both the porous nickel and its corresponding nickel oxide electrode obtained by electrochemical oxidation method as electrode materials. We have studied and characterized both the symmetric and asymmetric supercapacitor cell assemblies based on the porous nickel and NiO electrodes using cyclic voltammetry, electrochemical impedance spectroscopy and charge-discharge analysis. In all these cases, we have used activated carbon having a high specific surface area as a negative electrode. We have obtained a specific capacitance value of 473 F/g (for single electrode) for the porous nickel electrode. We have determined the response time of 0.65ms and 160ms for the
supercapacitor cell assemblies based on porous nickel and nickel oxide electrode materials respectively. This suggests the potential applications of these materials in short duration pulse devices. We observed that the measured ESR value is relatively high in the case of porous nickel supercapacitors due to the additional contribution from EDR arising out of the diffusion of ions through the pores and this can be minimized by optimizing the design of the supercapacitor cell assembly.

The second part of this chapter contains the details of experimental studies carried out for the evaluation of high surface area porous nickel as a hydrogen evolution catalyst. We have shown that the porous nickel can be used as a hydrogen-evolving cathode in electrocatalysis using Tafel plot analysis, which is the measure of current-potential characteristics of an electrode material. We have also compared the measured values of the porous Ni with the other existing Ni electrocatalysts such as sintered Ni, Raney Ni and nickel material obtained using HIPE template. From our experimental results, we find that the current density per geometric area and current density per unit mass of deposited Ni for the high surface area porous nickel is higher when compared to other nickel materials. The effective utilization of electrode true surface area with a good accessibility of electrolyte and wettability of surface of the porous nickel studied in the present work demonstrate the possible application of this material as a potentially good electrocatalyst.
Chapter 7: Summary of the work and scope for further studies

This chapter deals with the summary of some important experimental results and conclusions derived from our investigations of this thesis. We also briefly discuss the possibility and scope for future studies based on the results obtained from our research work in this chapter.
Based on our experimental investigation, we have arrived at some important conclusions that are listed below:

1. We have developed a new method of fabricating the high surface area nickel material using template electrodeposition based on the hexagonal liquid crystalline phase consisting of water, Triton X-100 and poly(acrylic acid) compositions.

2. We have obtained a roughness factor value of $3620$, the highest value reported for any electrodeposited nickel in literature, corresponding to a specific surface area of $650 \text{ cm}^2$ with a double layer capacitance of $338 \text{ mF/cm}^2$ for the template deposited nickel material.

3. We have shown that the application of an external magnetic field of $1 \text{ Tesla}$ at an angle of $45^\circ$ to the cathode surface during the electrodeposition of nickel results in the formation of nickel domains with spherical nickel nanoparticles mainly concentrated at the domain boundaries, in contrast to a layer type of growth observed in the absence of magnetic field.

4. From our studies on electron transfer reactions of redox probe molecules in surfactants self-aggregated systems, we find that the redox reaction of ruthenium(III)hexaammine complex is under charge transfer control in the micellar medium. In the case of microemulsion phase, the electron transfer reaction of potassium ferro/ferri cyanide redox couple shows a charge transfer control process and exhibits a microelectrode array behaviour. We also find that the redox reaction of $[\text{Fe(CN)}_6]^{3-}\text{H}^+$ couple is under diffusion control and exhibits a peak shaped voltammogram in cyclic voltammetry when the liquid crystalline phases are used as an electrolytic medium. This has been attributed to different diffusion processes (linear or radial) of redox species in the aqueous domains of the respective phases.
5. We have studied and characterized the structure, adsorption kinetics and barrier properties of self-assembled monolayer of 2-naphthalenethiol on gold surface for the first time in literature. Based on our STM and FTIR results, we have proposed a $\sqrt{3} \times 3 R \ 30^\circ$ overlayer structure with the naphthalene ring tiled from the Au surface normal for the monolayer of 2-naphthalenethiol on gold surface.

6. We have characterized and evaluated the barrier properties of self-assembled monolayers of liquid crystalline thiol terminated alkoxy cyanobiphenyl molecules having different chain lengths of $C_5$, $C_8$ and $C_{10}$ on Au surface for the first time in literature. We have shown that these SAMs on Au surface exhibit length dependent electron tunneling for ruthenium redox reaction.

7. From our studies, we find that the SAMs of aromatic thiols on Au surface show a very poor blocking ability and exhibit a predominantly diffusion controlled process for the redox reaction of ruthenium complex though the electron transfer reaction of potassium ferro/ferricyanide is significantly blocked. Based on the experimental analysis, we propose that the electron transfer reaction in the case of ruthenium redox couple takes place by a tunneling mechanism through the high $\pi$-electron density aromatic ring acting as a bridge between the monolayer-modified electrode and the ruthenium complex.

8. We have developed a new method of preparing self-assembled monolayers of thiol molecules on Au surface using a hexagonal lyotropic liquid crystalline phase consisting of a ternary mixture of water, Triton X-100 and the corresponding thiol compositions as an adsorbing medium. We find that the SAMs formed from the hexagonal liquid crystalline phase are highly compact, well-ordered, exhibit low ionic permeability with ultra low defect density and have excellent electrochemical blocking ability towards the
es when compared to that of corresponding SAMs prepared from commonly used organic solvents such as ethanol, acetonitrile and dichloromethane (conventional methods).

9. We have shown in this work that the high surface area porous nickel obtained using template electrodeposition can find potential application in supercapacitors as an electrode material and as a hydrogen-evolving cathode in electrocatalysis.

10. From our studies, we find that the supercapacitor cell assemblies based on the porous nickel electrodes exhibit a faster energy delivery capability at a higher power with a fast response time, which demonstrate the potential application in short duration pulse devices.
The publications in which the research studies carried out during this thesis work have been presented are listed below:

3. Assessment of liquid crystal template deposited porous nickel as a supercapacitor electrode material (Electrochemical and Solid-State Letters, 8(6), (2005), A308-312).
6. Self-assembled monolayers (SAMs) of alkoxycyanobiphenyl thiols on gold - A study of electron transfer reaction using cyclic voltammetry and electrochemical impedance spectroscopy (Journal of Colloid and Interface Science, Article in Press).
7. New symmetric and asymmetric supercapacitors based on high surface area porous nickel and activated carbon (Journal of Power Sources, Article in Press).

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8. Self-assembled monolayers of thiophenol, o-aminothiophenol and p-aminothiophenol on gold: effect of potential cycling and mixed SAM formation (Manuscript under preparation).

9. Self-assembled monolayers of alkoxy cyanobiphenyl thiols on gold prepared in a hexagonal lyotropic liquid crystalline phase – A study of electron transfer reaction using electrochemical techniques (Manuscript under preparation).