

CHAPTER 7

Summary of the work and scope for further studies

In this chapter, we summarize some of the important results and conclusions derived from this thesis work, which deals with the electrochemical studies and molecular self-assembly on surfaces using surfactant based systems as an electrolytic medium. We briefly discuss the possibilities and scope for future work based on the results obtained from our experimental work. Broadly, the research work that has been reported in this thesis can be classified as follows:

1. Preparation and characterization of high surface area materials such as nickel by template electrodeposition using the lyotropic hexagonal liquid crystalline phase and microemulsion phase as templates.
2. Studies involving the electron transfer kinetics using the self-aggregated structures of surfactants such as micelles, microemulsion phase and the lyotropic hexagonal liquid crystalline phase as electrolytic media.
3. Electrochemical studies and characterization of self-assembled monolayers (SAMs) of some aromatic thiols and alkoxybiphenyl thiols having different alkyl chain lengths on gold surface using organic solvents as an adsorbing media.
4. Studies on the barrier properties and interfacial properties of self-assembled monolayers (SAMs) of some aliphatic thiols, aromatic thiols and alkoxybiphenyl thiols having different alkyl chain lengths on gold surface using the lyotropic hexagonal liquid crystalline phase as an adsorbing medium.

5. Evaluation of high surface area porous nickel material obtained using template electrodeposition as an electrode material in supercapacitor applications and as a hydrogen evolving cathodes in electrocatalysis.

We summarize below the results and conclusions arrived from our experimental work that has been classified into the above-mentioned categories.

1. Preparation and characterization of high surface area materials such as nickel by template electrodeposition using the lyotropic hexagonal liquid crystalline phase and microemulsion phase as templates.

- We have used for the first time a new hexagonal lyotropic liquid crystalline phase consisting of a ternary system of water, Triton X-100 and poly(acrylic acid) and a binary system of water and Triton X-100 components as template.
- We have prepared a high surface area porous nickel material having a roughness factor of 3620, the highest value reported for any electrodeposited nickel in literature with a double layer capacitance of 338 mF/cm² using the template electrodeposition.
- We have shown that the high surface area arises essentially from the flooded pear shaped porous structure and densely distributed nanoparticles within as well as in between the pores.
- The surface morphology of the porous nickel material was characterized using SEM, STM and XRD. The properties and electrochemical activity of this material were evaluated by electrochemical techniques such as CV, EIS and Tafel plot analysis.

- We have studied the effect of applied magnetic field on the electrodeposition of nickel and its surface morphology.
- In contrast to a layer type growth obtained in the absence of field, a domain growth with nickel nanoparticles mainly concentrated at domain boundaries was observed in presence of an applied magnetic field of 1 Tesla during the electrodeposition of nickel.
- A large lowering of overpotential due to increase in the rate of metal deposition brought about by enhanced mass transfer induced by magnetic field was observed.
- A negative shift in the rest potential due to 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 magnetic field was also observed.
- We have also carried out the template electrodeposition of nickel using a microemulsion phase consisting of water, Triton X-100 and toluene compositions as a template.
- In this case, we have obtained a fractal growth of nickel surface having the particles of size ranging from $1\mu\text{m}$ to $2\mu\text{m}$ and there is no porous structure formation.

2. Studies involving the electron transfer kinetics using the self-aggregated structures of surfactant such as micelles, microemulsion phase and the lyotropic hexagonal liquid crystalline phase as electrolytic media.

- We have studied the electron transfer kinetics of redox probe molecules such as $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ redox couples using the self-aggregated structures of surfactant molecules as an electrolytic medium.
- We have used several self-aggregated structures of surfactant molecules such as micelles formed from sodium dodecyl sulphate (SDS), a microemulsion phase formed from a ternary mixture of water, Triton X-100 and toluene and water, Triton X-100 and p-Xylene, a hexagonal liquid crystalline phase and a lamellar phase consisting of a ternary mixture of water, Triton X-100 and decanol compositions.
- 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 $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple in the microemulsion phase using the electrochemical techniques such as cyclic voltammetry and electrochemical 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, microemulsion phase exhibits the microelectrode array behaviour for the redox reaction due to the radial diffusion of species in the aqueous micro domains formed by the surfactant molecules.
- In the case of liquid crystalline phase that has been used as an electrolytic medium, the electron transfer reaction is completely allowed indicating that the process is fully diffusion controlled.

3. Electrochemical studies and characterization of self-assembled monolayers (SAMs) of some aromatic thiols and alkoxybiphenyl thiols having different alkyl chain lengths on gold surface using organic solvents as an adsorbing media.

- ◆ We have studied the monolayer formation and characterization of some aromatic thiols such as 2-naphthalenethiol (NT), thiophenol (TP), o-aminothiophenol (o-ATP) and p-Aminothiophenol (p-ATP) on Au surface using ethanol as a solvent.
- ◆ Similarly, we have also studied and characterized the monolayers of alkoxybiphenyl thiols having different chain lengths of C₅, C₈ and C₁₀ on Au surface using dichloromethane as a solvent.
- ◆ The structure and orientation of thiol molecules in these monolayers have been characterized using grazing angle FTIR spectroscopy and scanning tunneling microscopic studies.
- ◆ The barrier properties and blocking ability of these aromatic monolayers have been evaluated by studying the electron transfer reactions of redox probe molecules such as potassium ferro/ferri cyanide {[Fe(CN)₆]^{3-/4-}} and hexaammineruthenium(III) chloride {[Ru(NH₃)₆]^{2+/3+}} on the SAM modified surfaces using cyclic voltammetry and electrochemical impedance spectroscopy.
- ◆ In the cases of SAMs of NT, TP, o-ATP and p-ATP on Au surface, we find that the monolayers exhibit a very poor blocking ability towards the redox reactions.
- ◆ We have tried to improve the blocking ability of these monolayers by a variety of processes such as potential cycling, annealing and mixed SAM formation.

- ◆ We find that although the redox reaction of potassium ferrocyanide complex is inhibited, ruthenium redox reaction is not at all inhibited in all these cases.
- ◆ 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.
- ◆ The distribution of pinholes and defects in these aromatic monolayers were analyzed by pinholes and defect analysis using their impedance data.
- ◆ Based on STM and FTIR studies we have proposed a new structure of $\sqrt{3} \times \sqrt{3}$ R 30° overlayer structure for the SAM of 2-naphthalenethiol on Au surface.
- ◆ We have also studied the effect of pH on the blocking ability of the monolayers of aminothiophenols on Au surface.
- ◆ In the case of SAM of alkoxycyanobiphenyl thiols on Au surface, it is found that these molecules mediate electron transfer between the Au electrode and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ redox couple when the alkyl chain length is shorter (C_5) and inhibit the process when the alkyl chain length is longer (C_8 & C_{10}).
- ◆ In all these cases of aromatic SAMs, we have obtained a surface coverage value of >99.9% for the monolayer on Au surface.

4. Studies on the barrier properties and interfacial properties of self-assembled monolayers (SAMs) of some aliphatic thiols, aromatic thiols and alkoxybiphenyl thiols having different alkyl chain lengths on gold surface using the lyotropic hexagonal liquid crystalline phase as an adsorbing medium.

- ✱ We have described a new method of preparing self-assembled monolayers (SAMs) using a lyotropic hexagonal liquid crystalline phase containing water, Triton X-100 compositions as an adsorbing medium.
- ✱ We have studied and characterized the monolayer formation of aliphatic thiols namely decanethiol and hexadecanethiol, aromatic thiols such as 2-naphthalenethiol, thiophenol and p-aminothiophenol and alkoxybiphenyl thiols having different chain lengths of C₅, C₈ and C₁₀ on Au surface using the above-mentioned hexagonal liquid crystalline as an adsorbing medium.
- ✱ We have also compared our results with that of the corresponding monolayers obtained using organic solvents as adsorbing media.
- ✱ The stability and blocking ability of these monolayers were characterized using grazing angle FTIR spectroscopy and electrochemical techniques.
- ✱ Cyclic voltammetry and electrochemical impedance spectroscopy were used to evaluate their barrier properties and insulating properties by studying the electron transfer reactions of redox probe molecules viz., {[Fe(CN)₆]^{3-/4-}} and {[Ru(NH₃)₆]^{2+/3+}} redox couples on the SAM modified electrodes.
- ✱ 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.

- ✱ 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.
- ✱ In the case 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 as an adsorbing medium.
- ✱ We have ruled out the multilayer formation and co-adsorption of surfactant molecules on Au surface using grazing angle FTIR spectroscopy and capacitance measurements.
- ✱ Impedance spectroscopy data were used to determine the charge transfer resistance (R_{ct}), which is the measure of blocking ability of the monolayer, surface coverage of the monolayer on Au surface and pinholes and defects analysis to find out the distribution of pinholes in the SAM.
- ✱ Our results suggest that the SAMs of very low defect density and extremely low ionic permeability can be obtained when a hexagonal liquid crystalline phase is used as an adsorbing medium.
- ✱ 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.
- ✱ We have also proposed a possible mechanism for the monolayer formation using the hexagonal liquid crystalline phase as an adsorbing medium.

5. Evaluation of high surface area porous nickel material obtained using template electrodeposition as an electrode material in supercapacitor applications and as a hydrogen evolving cathodes in electrocatalysis.

- ✦ We have shown that the high surface area porous nickel material fabricated using the template electrodeposition can be a possible source of applications in supercapacitors as an electrode material and as a hydrogen-evolving cathode in electrocatalysis.
- ✦ We have studied and evaluated both the symmetric and asymmetric supercapacitor cell assemblies based on the porous nickel and its corresponding NiO electrodes using cyclic voltammetry, electrochemical impedance spectroscopy and charge-discharge analysis.
- ✦ In all these cases, activated carbon having a high specific surface area was used as a negative electrode.
- ✦ We have obtained a specific capacitance value of 473 F/g for a single electrode of porous nickel material.
- ✦ 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.
- ✦ 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.
- ✦ Our results based on the experimental studies indicate the potential application of these materials in short duration pulse devices.
- ✦ We have also shown that the high surface area porous nickel can be used as a hydrogen-evolving cathode in electrocatalysis using Tafel plot analysis and

comparative studies with other existing nickel electrocatalysts such as sintered Ni, Raney Ni and nickel material obtained using HIPE template.

- ✦ From these studies, 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 studied in this work is higher when compared to other materials that have been mentioned above.
- ✦ The effective utilization of electrode surface area of the porous nickel with a good accessibility of electrolyte and wettability of surface demonstrate the possible application of this material to perform as a good electrocatalyst.

Scope for future work

In chapter 3, we have discussed a new method of preparing the high surface area porous material such as nickel using template electrodeposition. We have used a new hexagonal liquid crystalline phase consisting of water, Triton X-100 and poly(acrylic acid) compositions as a template. We have obtained a specific surface area of 650 cm^2 , which corresponds to a roughness factor of 3620, the highest value reported for any electrodeposited nickel in literature. We have also shown the possible applications of this high surface area porous nickel material in supercapacitors and as a hydrogen-evolving cathode in electrocatalysis in chapter 6. We are aware that in addition to nickel there are a plenty of other catalytically important materials such as platinum (Pt), palladium (Pd), gold (Au), copper (Cu) and alloys of different metals can also be obtained using this template electrodeposition. Further, we have used a hexagonal liquid crystalline phase formed from the ternary mixture involving Triton X-100 surfactant molecule. The template electrodeposition using other liquid crystalline phases and also a variety of phases formed by other surfactant

molecules such as Tween-20, AerosolOT, SDS and CTAB etc., can also be performed.

Similarly, in chapter 5, we have discussed about a new method of preparing the self-assembled monolayer on Au surface using a lyotropic hexagonal liquid crystalline phase as an adsorbing medium. We find from our experimental results that the monolayers formed from the hexagonal liquid crystalline phase exhibit excellent electrochemical blocking ability towards the redox probes, having a very good insulating properties and show a highly ordered, structurally well-oriented, dense, compact film with ultra low defect density when compared to the corresponding SAMs obtained using organic solvents as an adsorbing medium possibly due to the entrapment of small organic solvent molecules in the latter case. The other phases formed by the self-assembly of surfactant molecules such as reverse hexagonal liquid crystalline phases, microemulsion phases can also be used as an adsorbing medium for monolayer preparation and it will be interesting to study the barrier properties and structural organization of these monolayers on Au surface. The monolayer preparation and its characterization using a variety of other liquid crystalline phases formed by other surfactant molecules can also be studied.

We have shown in this work that the electron transfer reaction of ruthenium complex is not significantly inhibited on some aromatic thiols coated Au electrodes. This shows the possibility of using aromatic thiols modified Au electrodes in bio-sensors with $[\text{Ru}(\text{NH}_3)_6]^{2+|3+}$ complex as a redox mediator. The possible advantage of such an approach is the elimination of surface heterogeneity and bio-fouling.