

Electrical and Optical Investigations on Polymer-Metal Oxide Composite Thin Films prepared by Langmuir Blodgett Technique

*A
Thesis
Submitted for the Award
of the Degree of*

DOCTOR OF PHILOSOPHY

By

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October 2015

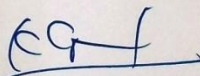
DEDICATED

**To my parents and my husband Er. Gurtej Singh Sahota for
supporting me all the way!**

THAPAR UNIVERSITY, PATIALA

CERTIFICATE

This is to certify that the thesis entitled **“Electrical and Optical Investigations on Polymer-Metal Oxide Composite Thin Films prepared by Langmuir-Blodgett Technique”** submitted by **Gurpreet Kaur Bhullar**, for the award of the degree **DOCTOR OF PHILOSOPHY** of THAPAR UNIVERSITY, Patiala, Punjab, India, is a record of the study conducting by her under my supervision and guidance. The subject matter of this dissertation has not been previously published or submitted to any other university for the award of any other degree, diploma, associateship, fellowship or any other similar title.



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ACKNOWLEDGEMENTS

This thesis is towards the partial fulfillment of the requirement for the degree of Doctor of Philosophy (Physics). This work would not have been completed without the help and guidance of my revered guide, respected teachers, colleagues and family members. I would like to thank all those people who made this thesis possible.

I consider myself to be most privileged to express deep gratitude and thanks to my supervisor **Dr. K.K. Raina, Distinguished Professor, School of Physics and Materials Science, Thapar University, Patiala**. This work has been possible with his consistent supervision, encouragement and support. Under his guidance, I successfully and smoothly overcame every hurdle and learned a lot. He encouraged me to improve my presentation skills and pursue for good quality research work. In spite of his busy schedule, he always encouraged academic discussion. I feel indebted to him for everything that I have learnt from him.

I express my sincere thanks to **Dr. Puneet Sharma** and my PhD progress committee members, **Dr. Manoj K. Sharma (Head SPMS & Prof.)**, **Dr. Kulvir Singh**, **Dr. D.P. Singh** and **Dr. H. Bhunia** for their useful suggestions and comments during my progress report presentations.

My sincere thanks to **Prof. O. P. Pandey (Dean, Research and Sponsored Projects)** for the various encouraging lectures during the course work classes.

My special thanks go to **Miss L.K. Brar** for her help and support at many stages of work. I am highly thankful to her for providing training to operate LB and AFM.

I acknowledge **the University Grants Commission, Delhi** for their financial support as a '**UGC SRF Fellow**' under **MANF** scheme.

I am also thankful to all **Staff of SPMS**, Thapar University, Patiala for their helping nature throughout my research work.

My special thanks go to my friend **Mrs. Ramneek Kaur** for her great sense of co-operation throughout my Ph.D. work. We worked collectively and sort out many issues regarding data analysis.

My sincere thanks go to my seniors **Dr. Pankaj Kumar**, **Dr. Parveen Malik**, **Dr. Ravi Shukla**, **Dr. Parveen Kumar**, **Dr. Rekha** and **Dr. Renu** for their support and encouragement.

I am also thankful to my colleagues **Dr. Rishi Kumar**, **Mrs. Manju Middha** and **Dr. Dipti** at

the Materials Research Laboratory for having maintained a congenial, competitive lab atmosphere and providing a stimulating fun filled environment. Last but not least, I place a deep sense of gratitude to *my parent Mrs. Jasbir kaur and Mr. Gurcharan Singh Bhullar, my sister Manjot Kaur, my brothers Shabdel Singh Bhullar, Jaskarn Singh, Amrik Singh, my neice Armin Kaur, my daughter Japleen Kaur, my aunt Hardeep Kaur Sahota and my Husband, Er. Gurtej Singh Sahota* for their sincere encouragement, being a source of inspiration throughout my research. I have no words to express thanks for their love, blessings and unconditional support in all circumstances.



Dated 17June 2016

Gurpreet Kaur Bhullar

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List of Publications

Journal Publications

SCI Journals

- 1) Bhullar G.K., Kaur R., Raina K. K. **“Hybrid Polyaniline–TiO₂ Nanocomposite Langmuir–Blodgett Thin Films: Self-Assembly and Their Characterization”** J. App. Poly. Sci. 2015, **132 (5):** 1-7.
- 2) Bhullar G.K., Kaur R., Raina K.K. **“Growth, Morphology and Electrical Characterization of Polyaniline–ZnO Nano-Composite Langmuir Blodgett thin Films.”** Journal of Electronics Materials. 2015, **44 (10)**, 3422-3429
- 3) Bhullar G.K., Kaur R., Raina K.K., **“Electrical Characterization of Polyaniline–ZnO nano composite Langmuir Blodgett thin film by Conductive Atomic Force Microscopy.”** MRS Spring Meeting Proceedings, Cambridge University Press, 2014, **1668**, mrss14-1668.
- 4) Bhullar G.K., Kaur R., Raina K.K. **“Formation of Nanostructures of Polyaniline–TiO₂ nano-composite, CAFM Analysis, electrical properties.”** (Communicated, Polymer)

Other related publications

- 5) Kaur R., Bhullar G.K., Raina K.K. **“Behaviour of an ultrathin ferroelectric liquid crystal Langmuir–Blodgett film at an air–water and air–solid interface”.** Liq Cryst. 2012, **39**, 1375–1380.
- 6) Kaur R., Bhullar G. K., Rao N. V. S., Raina K. K. **Effect of pH on the control of molecular orientation in monolayer of bent-core liquid crystal materials by Langmuir–Blodgett method.** Liq Cryst. 2014, **42(1)**, 8-17.

7) Kaur R., Bhullar G.K., Raina K.K. **“Effects of silver nanoparticles doping on morphology and luminescence behavior of ferroelectric liquid crystals Langmuir-Blodgett films. ”**. Liq Cryst. 2016, DOI:10.1080/02678292.2016.1200678

Non-SCI Journals

1) Bhullar G.K., Kaur R., Raina K.K. **“Investigations on polyaniline–TiO₂ nano-composite Langmuir Blodgett thin films.”** AIP Conf. Proceed. 2013, **1536**, 491-492.

2) Bhullar G.K., Raina K.K., **“Surface Potential Studies of Langmuir Monolayers of Polyaniline-TiO₂ nano-composite”** AIP Conf. Proc. 2014, **1591**, 972-974.

Other related publications

3) Kaur R., Bhullar G.K., Raina K.K. **“Surface viscoelastic properties of spread ferroelectric liquid crystal monolayer on air-water interface”** AIP Conf. Proceed. 2013, **1536**, 1377-1378.

List International/National Conference

International Conferences

[1] “Studies of Langmuir Blodgett films of Polyaniline –TiO₂ composites”

Bhullar G.K., Kaur R., Raina K. K. **International Workshop on Soft Matter Chemistry**, RRI Bangalore, (9-11.November.2011), pp85

[2] “Investigations on Polyaniline TiO₂ nano-composite thin films prepared by Langmuir Blodgett technique”

Bhullar G.K., Kaur R., Raina K. K. **24th International Liquid Crystal Conference**, Mainz, German, (19-24.August. 2012). Abstract-reference code: 5551_0476

[3] “Optical and Morphological Study of Ferroelectric Liquid Crystal Langmuir-Blodgett Films”

Kaur R., Bhullar G.K., Raina K.K. **16th International workshop on physics of semiconductor devices**, IIT Kanpur (19-22. December. 2011), DL P.04

[4] “Investigation on Polyaniline-TiO₂ nano-composite Langmuir Blodgett Thin film”

Bhullar G.K., Kaur R., Raina K. K. **International Conference on Recent Trends in Applied Physics & Material Science**, Govt. College of Engineering & Technology , Bikaner. (1-2 February. 2013). D-1444, pp 151.

[5] “Investigations of Polyaniline-ZnO nano-composite Langmuir Blodgett films at Air-Water and Air-Solid Interface”

Bhullar G.K., Kaur R., Raina K. K. **Organic Devices: The future Ahead (ODeFA-2014)**, BARC, Mumbai. (3-6. March. 2014). CP-64.

[6] “Electrical Characterization of Polyaniline-ZnO nano composite Langmuir Blodgett thin film by Conductive AFM”

Bhullar G.K., Kaur R., Raina K. K. **2014 MRS Spring Meeting and Exhibit, San Francisco**, (21-25 April 2014) pp C6.17

National Conferences

- [7] “Formation of polyaniline-ZrO₂ nano-composites using Langmuir - Blodgett technique”
Bhullar G.K., Kaur R., Raina K. K. **National Symposium on Radiation Physics and Nano-materials (NSRPN-11)**, Punjabi University, Patiala (4-5. February. 2011). pp NP7.
- [8] “Systems for Langmuir-Blodgett films a unique tool for molecular electronics”
Bhullar G.K., Kaur R., Raina K. K. **National Seminar on Advanced Materials and Devices**, G.V.M. Girls college Sonapat (3-4. July 2011). CP59, pp 80.
- [9] “Morphological studies of Langmuir Blodgett thin films of polyaniline-TiO₂ composite material”
Bhullar G.K., Raina K. K. **23rd AGM MRSI 2012**, Thapar University Patiala (13-14. February. 2012). pp 160. (**Best Poster Prize**).
- [10] “Studies on Langmuir Blodgett Films of Poly(dimethylsiloxane-co-alkylmethylsiloxane)”
Bhullar G.K., Kaur R., Raina K. K. **National conference on Recent trends in material Science research**, NIT Srinagar, (3-5 September, 2012).
- [11] “Investigation on Polyaniline - ZnO nano composite Langmuir Blodgett thin films”
Bhullar G.K., Kaur R., Raina K. K. **19th National Conference on Liquid Crystals (NCLC-19)**, Thapar University, Patiala, (21-23, November. 2012) pp. 89.
- [12] “Surface Potential Studies of Langmuir Monolayers of Polyaniline-TiO₂ nano-composite”
Bhullar G.K., Raina K. K. **58th DAE- Solid State Physics Symposium** at Thapar University, Patiala, (17-21. December. 2013). F-211

List of Awards

- **Best poster presentation** awarded at AGM MRSI 2012, pp 156, Thapar University Patiala, 13-14 February 2012 for the poster entitled “**Morphological studies of Langmuir Blodgett thin films of polyaniline-TiO₂ composite material**” presented by **Gurpreet Kaur Bhullar**, Ramneek Kaur and K.K. Raina.
- **The Diwan Jawaharlal Nayer memorial prize** awarded at 19th National Conference on Liquid Crystals (NCLC-19), November 21-23, 2012 for the poster entitled “**Langmuir monolayer of Bent-Core liquid crystal formed by changing sub phase pH**” presented by Ramneek Kaur, **Gurpreet Kaur Bhullar** and K.K. Raina.

PREFACE

We have prepared polymer and its nano-composite systems with metal oxides by chemical route and then prepared their homogenous LB films. Interaction between nanoparticles and host polymer matrix resulted in phase changes of monolayer. Orientation and ordering of polymer at air-water interface have been significantly improved by adding nanoparticles into it. These materials are characterized for electrical, optical, structural, thermal and morphological properties. It has improved many physical properties of polymer matrix like morphology, electrical and optical properties. Local Current-voltage (I-V) spectroscopy results by C-AFM show semiconducting behaviour of PANi and its nano-composite LB films and conductive data images show almost uniform current distribution through the films. These LB films have opened up opportunities for understanding of many properties for application point of view.

The proposed objectives were:

1. To prepare composite materials of polymer systems with metal oxides.
2. Optimization of physical parameters for growing appropriate Langmuir Blodgett Films.
3. To characterize these materials for electrical, optical, thermal, structural and morphological properties.

The brief summary of the chapters is as follows:-

Chapter 1 conveys the importance of studies carried out. This chapter contains an introduction to polymers and nano-composites. This is followed by a discussion on Langmuir Blodgett technique. An overview of physical properties of conducting polymer PANi is given on the basis of their molecular arrangement and oxidation states. The required amphiphilicity of PANi is provided by the presence of -NH- groups, benzoid and quinoid rings in a polymer chain.

Chapter 2 explains about Langmuir-Blodgett (LB) experimental set up and steps involved in deposition of LB films. Langmuir monolayers at air-water interface are characterized by π -A isotherm (Pressure-Area isotherms) which provides information of the phase transformations in the monolayer during constant compression process. Temperature controller is used for monolayer stabilization and thermal variations in monolayer phases are examined at different temperatures. UV-VIS and FT-IR Spectroscopy provides information about bonds present in LB film structure. XRD provide insights to the molecular arrangement of films. We also discuss the imaging method atomic force microscopy (AFM) in non-contact mode as well as in contact

mode for topographical imaging of transferred films onto a solid support. Conductive atomic force microscopy (C-AFM) provide local I-V characteristics and conductive data imaging.

Chapter 3 It describes about formation of polyaniline (PANi) LB films and optimization of various physical parameters for growing appropriate Langmuir monolayers at air–water interface and depositing Langmuir Blodgett films onto solid substrates. Polyaniline (PANi) has special characteristic due to the presence of reactive –NH– groups in a polymer chain, which imparts hydrophilic character to the system as well as relatively high conductivity and good chemical stability. Surface pressure–area (π -A) isotherms show phase transformations in the monolayer during compression process. Langmuir–Blodgett films of PANi show that the interaction between molecules in the monolayer was increased during barrier compression, resulting in increased surface pressure. Surface potential and dipole moment of Langmuir monolayer of PANi increases with temperature and becomes +ve at room temperature and decreases after 30 °C. Langmuir–Blodgett thin films of PANi were deposited on the quartz and indium tin oxide coated conducting glass substrates. Fourier transfer infrared spectroscopy and UV–visible spectroscopy study indicates formation of PANi, whereas X-ray Diffraction study show the presence of broad peaks (of less intensity) of the synthesized PANi situated at $2\theta = 21.23^\circ$ and 25.15° . Atomic force microscopy shows average height profile of 25 nm. Local Current-voltage (I-V) spectroscopy results by C-AFM show semiconducting behaviour of PANi LB film and conductive data images show almost uniform current distribution through the PANi LB films.

Chapter 4 contains LB film formation of Polyaniline (PANi)–titanium dioxide (TiO₂) nano-composite (5, 10, 15, and 20) wt % materials prepared by chemical polymerization of aniline doped with TiO₂ nanoparticles. Surface pressure–area (π -A) isotherms of these nano-composites show phase transformations in the monolayer during compression process. Surface Potential and dipole moment increases with increase in temperature and after 35 °C again decreases due to increase in entropy. FTIR spectroscopy and UV–visible spectroscopy study indicates the presence of TiO₂ in PANi, whereas X-ray Diffraction study confirmed the anatase phase of TiO₂ and particle size (~nm) of PANi–TiO₂. AFM images in non-contact mode as well as in contact mode revealed the inclusion of TiO₂ in the polymer matrix in the form of nanometer-size grains. LB films shows that these are formed from nanometer-size grains. C- AFM show local I-

V characteristics and conductive images. This work is highly useful for sensor device fabrication technology.

Chapter 5 presents Polyaniline–Zinc oxide (5, 10, 15, and 20) wt % nano-composite materials prepared by chemical route. Surface Pressure-Area (π -A) isotherms of PANi–ZnO nano-composite show phase transformations of monolayer during compression process. PANi–ZnO nano-composites show good surface properties at air-water interface. Stable monolayers are formed at air-water interface which are efficiently transferred to solid substrate as ultrathin films by Langmuir-Blodgett technique. Thermal properties were studied at (10, 15, 20, 25, and 30) °C. UV-Visible spectroscopy showed that the electronic structure of PANi is modified with addition of ZnO in to PANi matrix. FTIR confirms chemical functionalization. The topography showed the presence of ZnO nanoparticles in the polymer chains. Local Current-voltage (I-V) spectroscopy results show that there is increase in current range in case of PANi-ZnO nano-composite LB film as compared to PANi LB film. Conductive data images are recorded to probe charge transport current in homogeneities in LB films and show almost uniform current distribution. These results would make them promising films for their applications in molecular nanoelectronic devices.

Chapter 6 contains summary of the work. It shows that LB technique provide a novel method to develop ultrathin films. Future scope of work is also proposed here for developing sensor and molecular electronic devices.

CHAPTER 1

Polymer-metal oxide nano-composites and Langmuir-Blodgett Technique

Overview

In this chapter an overview of physical properties of conducting polymer polyaniline (PANi) and its nano-composites with metal oxide nanoparticles like titanium dioxide (TiO_2) and zinc oxide (ZnO) is given on the basis of their oxidation states and molecular arrangement. This is followed by a discussion on Langmuir-Blodgett technique. Amphiphilic character of polymer molecules which is necessary for LB film formation is discussed briefly. The required amphiphilicity of PANi is provided by the presence of -NH- groups, benzoid and quinoid rings in a polymer chain. Langmuir monolayer and Langmuir-Blodgett film formation at air-water interface in the constant compression mode of barriers is also discussed.

Introduction

1.1 Polymers

Polymers have a vital role in various fields of daily life due to their advantages, like flexibility, lighter weight, economical production and easy processability over conventional materials. In the early days of plastic technology, polymers were regarded as insulators but their microscopic structure and molecular dynamics analysis contributed a lot to the development of conductive polymers [1].

In recent years, conducting polymers have emerged as novel electronic materials considering their use in molecular electronic devices. Conjugated polymers or intrinsically conducting polymers (ICPs) or electroactive polymers are the organic polymers which conduct electricity [2]. These compounds may have conductivity in the range of either metals or comparable to that of the semiconductors. The electrical properties of conducting polymers can be manipulated by organic synthesis [3] and by advanced dispersion techniques [4]. Conducting polymers thus have an important role to play in the emerging field of science and technology.

In 1958 Natta et al. synthesized a conducting polymer known as polyacetylene. Depending upon its process of synthesis, this black coloured powder was found to be a semiconductor having conductivity in the range between 7×10^{-11} and $7 \times 10^{-3} \text{ Sm}^{-1}$.

Undoped polyacetylene was silvery, intractable and insoluble having conductivity comparable to that of semiconductors. Further investigations showed that when it is oxidized by halogens for example, iodine its conductivity increased almost a 10^8 to 10^9 times. In 1977, this wonderful observation about this doped polymer named, polyacetylene was reported by H. Shirakawa et. al. and they were honored with the 2000 Noble Prize in chemistry [5]. This proved the realization of an idea that a plastic can conduct electricity under specific conditions.

At the end of 1970s, organic conductive polymers attracted the interest of many researchers as they perceived that this class of materials perhaps could be processed by using traditional plastic technology. Polymers are insulators due to the covalent bonds between atoms in the polymer chain. As the molecules are covalently bonded in polymer chains, there is hardly any chance of offshoring of the valence electrons. The availability of charge carriers and the path for their

movement is also very sparse. The conjugated molecules of carbon compounds may be conducting, as the electrons can delocalize via interaction of π -bonded electrons.

Conductive polymers can be differentiated into two categories: Filled polymers and Inherent conductive polymers (ICP). Some of the ICP polymers like, Polyaniline (PANi), Polypyrrole, Polyvinylene and Polythiophene possess quite reasonable conductivity.

Conducting polymeric materials have received increasing interest as alternatives to inorganic semiconductors. Conducting polymers are being used for the fabrication of various biomolecular electronic devices such as microactuators and biosensors [6, 7]. Due to their room-temperature operation, low fabrication cost, ease of deposition onto a wide variety of substrates, and rich structural modification chemistry [8-10], conducting polymer thin films find application in various kinds of sensors [11-12].

Preformed polymers have the capacity to self-assemble into hierarchical structures, due to the supramolecular interactions such as ionic, van der Waals, coordination and hydrogen bonding. In Comb-shaped polymers, the amphiphilic molecules are either covalently or physically bonded to the polymer backbone. The self-assembled structures are controlled by the interactions between the polymer backbone and adhered molecules. Conjugated polymers can be functionalized with amphiphiles to form self-organized structures.

1.2 Polyaniline

Amongst the various ICPs, polyaniline (PANi) is a semi-flexible rod polymer family having fantastic processability, high yield of polymerization and is relatively inexpensive, therefore it is one of the most sought after candidate for technological applications. It is fastly replacing the conventional materials because of its fascinating electrical properties. Its technological use depends crucially on the reproducibility and control of the molecular and supramolecular architecture of the macromolecule via some simple methodology like organic synthesis.

In the early 1980s Polyaniline has rapidly become a subject of considerable interest for physicists, chemists, scientists and researchers because of the revelation of its high electrical conductivity. The general structure of Polyaniline is shown in Figure 1.1. It consists of alternating reduced and oxidized repeat units. Average oxidation state of PANi is denoted by $1-y$ whereas y determines the existence of each of the oxidation states of PANi as shown in Figure

1.2. Leucoemeraldine ($y = 1$) is the fully reduced oxidation state, pernigraniline ($y = 0$) is the fully oxidized state, and emeraldine ($y = 0.5$) is an intermediate oxidation state.

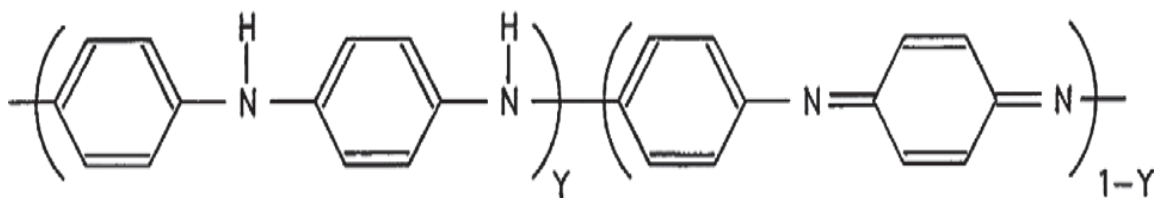


Figure 1.1: Structure of Polyaniline [13].

Polyaniline exists in several oxidation states with electrical conductivity varying progressively from 1^{-10} Scm^{-1} to 10 Scm^{-1} and even more. It is an organic semiconductor, prepared by the chemical or electrochemical oxidation of monomeric aniline. The course of the oxidation can be followed by monitoring changes in temperature or pH. Polyaniline exhibits both the electronic and ionic conductivity. The stability of Polyaniline at elevated temperature and in aggressive media is good. Emeraldine state of Polyaniline is conducting (Figure 1.3.) as neither the fully oxidized nor fully reduced states are conducting.

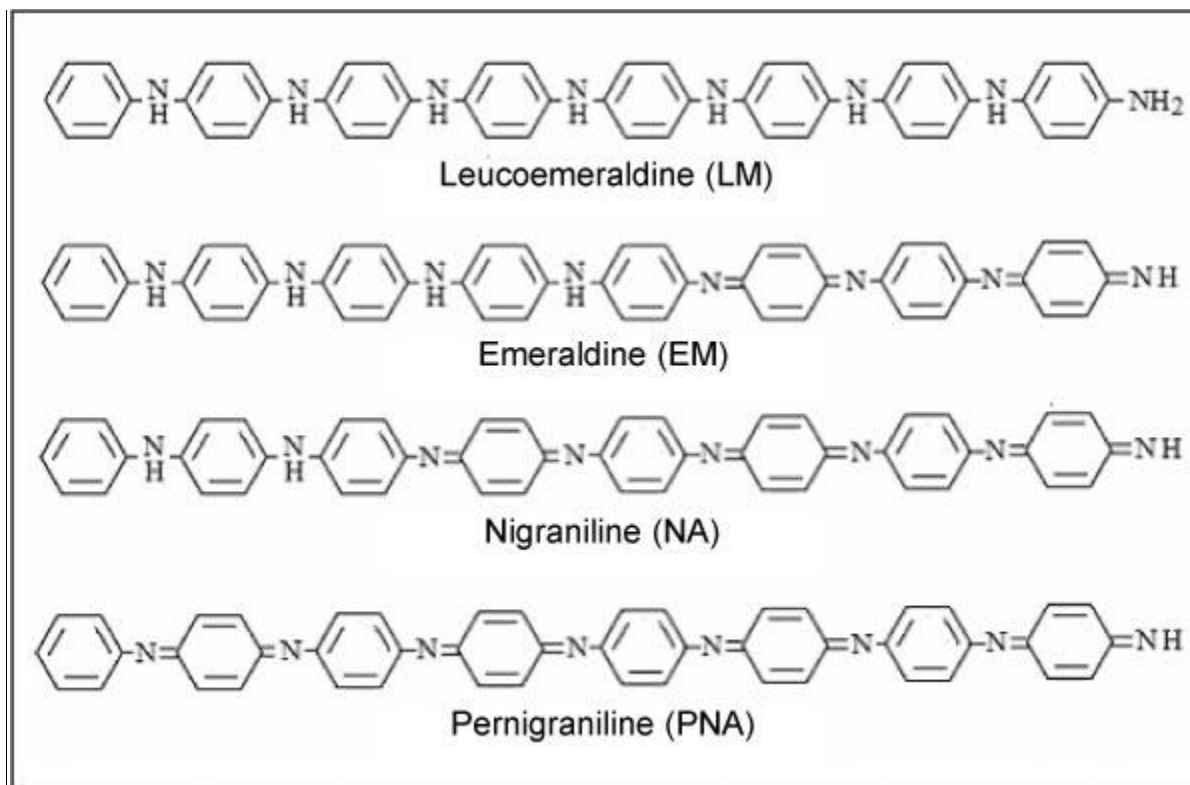


Figure 1.2: Oxidation states of Polyaniline [14].

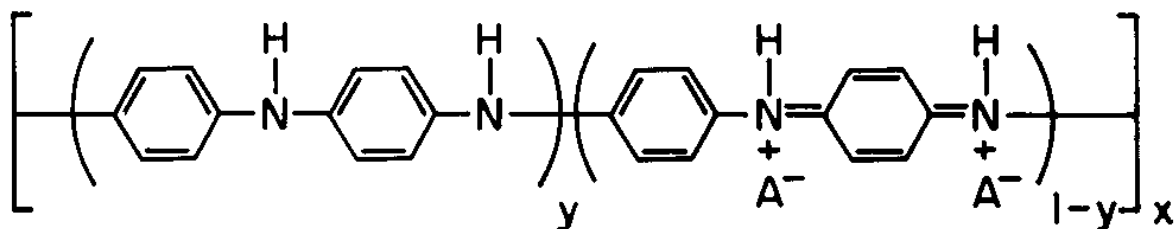


Figure 1.3: General chemical composition of conductive polyaniline [15].

In the conducting polymers the conduction mechanism and behaviour of charge carriers is based on the presence of delocalised polarons and protons. Polaron is a cation- radical that is partially delocalised over a polymer segment. This radical cation has a spin 1/2. It stabilizes itself by polarizing the medium around it. In case of a conjugated polymer when an electron is removed from the top of the valence band, a vacancy is created and unlike the classical band theory, it does not delocalize completely. Structural deformations are caused due to this partial delocalization that extends over several monomeric units. The energy level associated with this radical cation represents a destabilized bonding orbital and thus has a higher energy than the energies in the valence band. This rise in energy is similar to the one that takes place after an electron is removed from a filled bonding molecular orbital. Removal of another electron from the oxidized polymer containing the polaron, gives rise to two phenomena: Either this electron could come from a different segment of the polymer chain, thus producing another free polaron or from the first polaron level to create a dication called a bipolaron. Low doping levels produce polarons, whereas higher doping levels give rise to bipolarons. Bipolarons are doubly charged, but spinless. Structural deformations are also associated with the bipolaron. The polarons and bipolarons can move along the polymer chain by rearranging the double and single bonds in the conjugated system. High doping results in the formation of many bipolarons with their energies overlapping at the edges, creating narrow bipolaron bands in the band gap. Protonation is the basic mechanism for polyaniline (PANi) doping and is usually carried out by exposing the polymer to acidic substances shown in Figure 1.4.

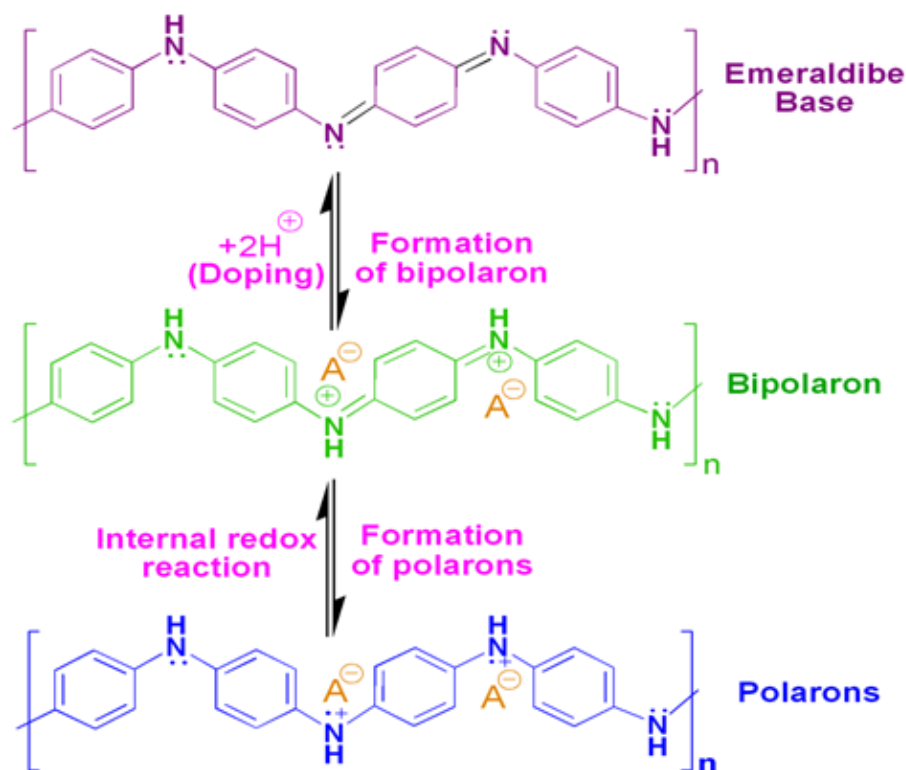


Figure 1.4: Protonation of polyaniline [16].

Controlled doping leads to enhancement of conductivity due to formation of charge carriers [16]. Conductive polyaniline in emeraldine form exhibit dark-blue colour in N-methylpyrrolidone (NMP) solutions which indicates protonic doping of polyaniline. Protonic doping is accomplished by treating synthesized PANi with acid. In the case of films doping is done either by dipping the emeraldine films in acid or by passing a gaseous acid over them, thus protonating the imine nitrogen atoms in the backbone of the polymer. The conductivity of polymers depends on the polymer synthesis method, purification techniques and physical treatment of the polymer etc. Electrical conductivity also increases with increasing degree of crystallinity.

Polyaniline can be synthesized easily by electrochemical or chemical oxidation of aniline in aqueous acidic media, using oxidants, such as ammonium peroxydisulfate ((APS) $(NH_4)_2S_2O_8$). Ammonium peroxydisulfate is crystalline, white, odourless salt. It is used as initiator for the polymerization of aniline and is a strong oxidizing agent in many applications like cleaning and picking of metal surfaces, bleaching formulation for hair cosmetics, production of binders and coating materials etc.

Chemical oxidation method is quite efficient for the synthesis of PANi nano-composites in comparison to electrochemical polymerization [17-19]. Chemical method is more effective for bulk synthesis of PANi and electrochemical method is more suitable for PANi thin films. Polymerization of aniline by chemical oxidation method has been extensively used for synthesizing polyaniline due to its ease and low manufacturing cost [20]. The advantage of chemical method lies in the fact that during this method PANi can have various morphological and electrochemical properties depending upon the synthesis conditions such as reaction temperature, stirring speed, reaction time, type of oxidant, type of solvent, dopant acid, surfactant and concentration of the reactants [21].

Polymerization of aniline is an exothermic process, So it is preferred to carry out polymerization at low temperatures with one reactant slowly added into the other under continuous stirring using magnetic stirrer. The aggregate morphologies of polyaniline include spheres, cylinders, disks, and vesicles. Depending on acidity conditions, polyaniline has globular, nanofibrillar or nanotubular morphology.

PANi find applications in coated fabric based microwave shields [22-25], biosensors [26], corrosion inhibitors [27], supercapacitors [28], in x-ray mask making [29] and as antistatic materials [30]. Among various polymers, polyaniline (PANi) is the most outstanding candidate for aforementioned applications because of its uncomplicated synthesis accomplishment as well as having ability to undergo reversible transformations from a conducting to a semiconducting form.

1.3 Polymer-Metal Oxide nano-composites.

Polymer-inorganic nano-composites have drawn attention due to their potential applications in numerous fields. Polymer composites are combinations of one or more inorganic nanoparticles with a polymer so that the unique properties of inorganic nanoparticles can be taken together with the existing qualities of the polymer. Nano-composite materials have more than one phase and at least one of the phases should have one dimension less than 100 nanometers [31]. These materials possess the electronic properties of semiconductors as well as the flexible behavior of polymers.

Alteration and enrichment of the properties of polymers occur through doping with several fillers such as organic-inorganic particles, metals, fibers, and semiconductors etc. This enables use

polymers as structural units. Polymers are doped with fillers due to the several reasons like enhanced processing, optical effects, density control and thermal conductivity, electrical properties and enhancement of mechanical properties, such as elasticity, hardness. The conductivity of the polymer relies upon the nature of dopant and the inorganic material's concentration, which plays an important role in conductivity of the nano-composites. There are several reports in literature about conducting polymers based inorganic–organic nano-composites because the inclusion of inorganic materials in the polymer matrix can introduce entirely new properties to the polymer. This can lead to new functional materials with the advantages of both the inorganic and the organic components [32-36].

Nano-composites of PANi are important candidates for device application in biosensors, gas sensors, optoelectronics etc. [37-40].

Nano-materials such as, metal-oxide nanoparticles, nano-structured conducting polymers and nanotube-polymer composites have elicited much interest among researchers owing to their applications in nano-level devices. Metal oxide and hybrid metal-oxide nanocrystals have great potential for electronic, optical and photocatalytic applications [41-43].

Titanium dioxide (TiO_2) nanomaterials have received great attention in the past few years due to their unique properties such as high chemical stability and high specific surface area [44, 45].

TiO_2 Nanoparticles has been studied intensively following the discovery of Honda–Fujishima effect [46] in 1972 due to its numerous possible applications in diverse fields like, photo-induced hydrophilicity, photocatalysis, dye-sensitized solar cells (DCCSs) etc. [47-49]. The photocatalysis based on transition metal–oxide semiconductor TiO_2 has been extensively used in the treatment of environment pollutants. Till date, TiO_2 has found the most suited one with highest activity because of its strong oxidizing ability, longtime thermal photostability, easily preparable in thin film form, non-toxic nature [50, 51].

TiO_2 nanotubes provide a large surface area to volume ratio, and their open capped structure is also suitable for sensor and detector applications [52]. The TiO_2 films are also being used for the development of self-cleaning and anti-fogging glass in future [53].

TiO_2 is one of the typical n-type semiconductors, while polyaniline is one of the typical conductive polymers and is usually considered as p-type material. In addition to it having good environmental stability and mechanical flexibility, its conductivity could be controlled with acid

or base. It has promising applications in several fields, for example, light-weight battery electrodes, electromagnetic shielding devices, anti corrosion coatings and sensors [54-59]. There is a reasonably good possibility of synthesis of new materials with integral behavior between PANi and TiO₂.

Despite the fact that a large number of studies on polyaniline–TiO₂ composite materials have been reported [60-62], very rare reports touched upon the behavior of Langmuir monolayer and LB films of PANi–TiO₂ nano-composite systems. Recently, organic–inorganic hybrid materials have been ultimately explored to have novel composites with interdependent or compatible behaviors with their prospective use in electronic or nanoelectronic devices [63-65].

In recent years, nanostructured zinc oxide (ZnO) semiconductor materials have aroused fundamental scientific interest due to their potential applicability in nanoscale electronic devices [66-68].

Among the noncentrosymmetric compounds, oxide materials, like zinc oxide (ZnO), have shown resistance switching behavior [69-71]. Moreover, ZnO is given due consideration as a material of technological and scientific significance because of its exclusive conductive, piezoelectric and optical properties.

ZnO is group II–VI semiconductor having a wide band gap of 3.37 eV [72-74]. PANi–ZnO nano-composite materials have been used in gas sensors and other heterostructure devices, but the behavior of Langmuir monolayer and LB films of PANi–ZnO nano-composite systems is still at infancy. PANi–ZnO nano-composite LB thin films still need to be explored for their structural, optical, topographical and local electrical properties.

Extremely organized films fabricated from polymer-metal oxide nano-composites can open new possibilities for the organic-inorganic hybrid materials for their application as semiconducting and metallic components in electronics. In organized films long-range crystal ordering along with the particular orientation of the π - π stacked chains on the film surface is crucial for charge transport control.

A great deal of attention has been focused on the synthesis and manufacturing of the nano-size objects based devices. The extremely organized, orderly arranged patterns of the nano-composite materials, can propose a wide range of applications from nanoscale electronics and optoelectronics to molecular level electronics. For the development of self-assembled structures,

Langmuir-Blodgett (LB) technique is well suited for the assemblage of nano dimensional materials, like the nano-composite, nanoparticles, nanorods and nanowires [75]. Polymeric LB films preparation can be done with two methods. In the first method, monomer moieties are polymerized on water surface, then compression with barriers result in organization on water subphase. The disadvantage of this method is that polymerization cause volume contraction and stress, which leads to cracking of the film. The second way is to directly produce LB film of preformed polymers. LB films prepared by this latter method do not require any further processing.

1.4 Ultrathin films

Nanoscale films produced with the LB technique are a type of ultrathin films. A nanofilm is an ultrathin film in the range of (1-100) nanometers. To understand ultrathin films, it is important to understand the orientation of molecules at air-water interface. The molecules are primarily either hydrophilic (water soluble) or hydrophobic (water insoluble). The hydrocarbon chains are hydrophobic part while the polar groups (like OH^- , NH_2^+) attribute to the hydrophilicity of the molecule [76]. The molecules which have covalently bonded hydrophilic and hydrophobic groups are termed as amphiphilics. The necessary condition for the formation of LB film is that the compound should be amphiphilic in nature, so that it can be spread on the water surface. Figure 1.5 shows the orientation and constituents of an amphiphile at the air-water interface [77]. Polar groups align toward water surface and non-polar groups stay upwards on air.

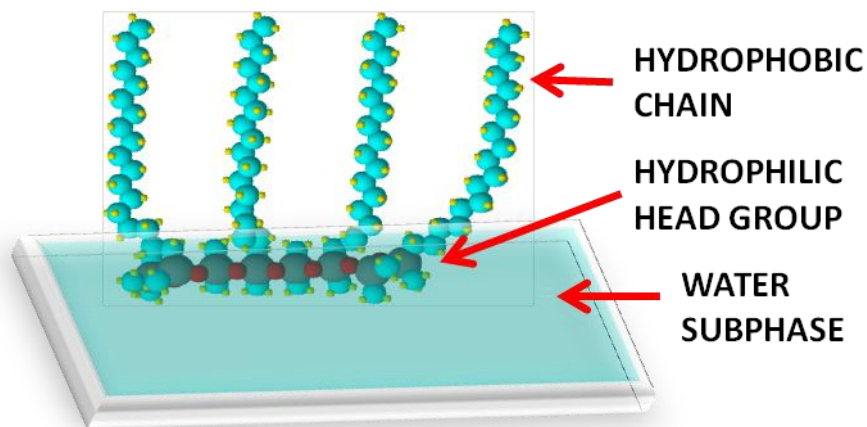


Figure 1.5: Schematic diagram of the orientation and constituents of an amphiphilic molecule at interface.

A single layer of amphiphilic or semi-amphiphilic molecules spread at the air-water interface is termed as Langmuir monolayer. In order to get a well-ordered Langmuir-Blodgett (LB) film, it is absolutely necessary to get a stable Langmuir monolayer at the air-water interface. Interfaces are the boundary regions separating bulk regions of matter, with the properties of two different phases across them influencing the behaviour of molecules lying in this region. The physical and chemical properties are influenced much by the composition, structure and morphology of material's surface depending upon the nature and bond strength at the interfaces [4]. So, nanostructuring of materials through LB technique has been efficiently used to explore the properties of the surface and to achieve well-designed surface morphologies. Well-designed polymers and polymer metal oxide nano-composite materials allow to observe new phenomena, which are not possible to observe in bulk materials because of structural restrictions.

Langmuir monolayers are transferred onto a solid surface by using LB technique. The overall effect of a Langmuir film on the water surface is the reduction of surface tension of water.

LB technique is a frequently used assembly approach with exquisite unique features like precise control of thickness, deposition homogeneity and reproducibility. Ordered monolayer can be formed over a large area, which can be easily deposited onto solid substrate and it is also possible to fabricate hybrid films by alternating monolayer or multilayer deposition. The final structures can also be manipulated through control of the compression process.

Substitution of other chemical groups (COOH, OH, NH₂) onto the benzene nucleus allows LB films based on cyclic aromatic to be built up. In benzene ring, the replacement of C by N renders the molecule more hydrophilic. In order to use the LB technique, the material should be insoluble in water.

1.5 Origin of Langmuir-Blodgett Films

Several molecular compounds have been analyzed at the air-water interface over the years, but Aristotle extensively studied the phenomenon of decrease in sea roughness caused by a thin film of oil dispersed on the sea surface [78]. The first scientific investigation of this effect was reported in 1774 by Benjamin Franklin. He carried out the experiment on the surface of a pond, in which he observed that the little amount of oil poured on the surface of water, made the waves hush and the pond smooth as a looking glass but he did not realize the formation of monolayer of oil over the water surface. At the end of the nineteenth century, Agnes Pockels described a method for manipulating oil film on water using barriers laid across the top of a trough. In her kitchen sink, she tried to compress layers of oils with barriers and proved that surface pressure would change with area confinement [79]. Lord Rayleigh in 1899 quantitatively measured the reduction of the surface tension of water due to spreading of oil and proposed that film was a single molecular thickness only. In 1917, a systematic study on these floating monolayers was done by Irving Langmuir [80]. Using Pockel's idea, he devised the surface balance and the Langmuir trough for the measurements [81]. His work in the field of surface chemistry fetched Nobel Prize for him in 1932. In 1935 Katherine Blodgett refined the method of transferring the floating monolayer onto the solid supports in order to build up multilayers by the successive deposition of monomolecular layers [82, 83]. These films are called Langmuir-Blodgett films. From the name of both great scientists these films are named as Langmuir-Blodgett (LB) films. Initially the LB technique was meant for amphiphilic molecules, but due to additive properties of LB films, many new materials comes in range e.g.: polymers, semi-amphiphilic materials [4, 84, 85]. Spectroscopic studies on LB films were carried out by Hans Kuhn. It moved LB to a new field of ultrathin films [86].

1.6 Monolayer Formation.

Langmuir monolayer is formed at the interface of air and water with constant compression mode of barriers. Molecules on the surface of the water are first organized into a monolayer array. Langmuir monolayers are necessary for the fabrication of a Langmuir-Blodgett film, which is multi or monolayers transferred from the liquid surface onto a solid substrate [87]. Investigations of Langmuir films have provided a bridge between physics, chemistry, biology and electronics. Constant motion of barriers results in uniform compression of the monolayer. The attractions between particles in the air-aqueous interface results in the aggregation of particles, thus, the particles become more stable in the air-aqueous interface. The LB deposition process is schematically shown in Figure 1.6. Depositing materials are dissolved in volatile organic material. Then very small (μl) quantities are spread dropwise on water surface. Spread molecules form a stable monolayer on air-water interface with compression of barriers. This compressed and well arranged monolayer is transferred onto a solid substrate.

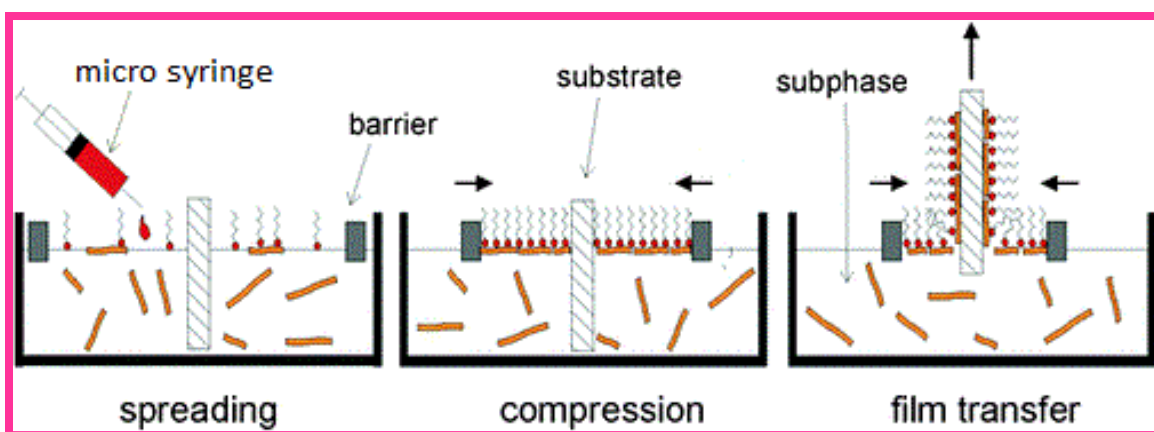


Figure1.6: Schematic of the LB deposition process [88].

1.7 Surface pressure – Area (II-A) Isotherm

Isotherm profile gives variation of surface pressure (Π) with reduction in surface area of film (A). Compression process of monolayer result in formation of well organized films after crossing through various phases. When dissolved material is spread on water surface, molecules are in gaseous 2-Dimensional (2D) phase as shown in figure 1.7. With increase in compression by movement of barriers molecules start interacting with each other. It results in formation of expanded 2D phase. In this phase hydrophilic part of molecules is attracted toward water surface

and hydrophobic groups are freely standing toward air, resulting in increase of surface pressure. Surface pressure of monolayer is measured by using this equation (1.1):

$$\Pi = \gamma_0 - \gamma \quad 1.1$$

Where Π represents surface pressure of monolayer and γ_0 is surface pressure of water without monolayer, γ represent surface tension due to monolayer. With further compression of barriers molecules reaches to condensed 2D phase. Compression beyond this point will result in collapse of monolayer pattern.

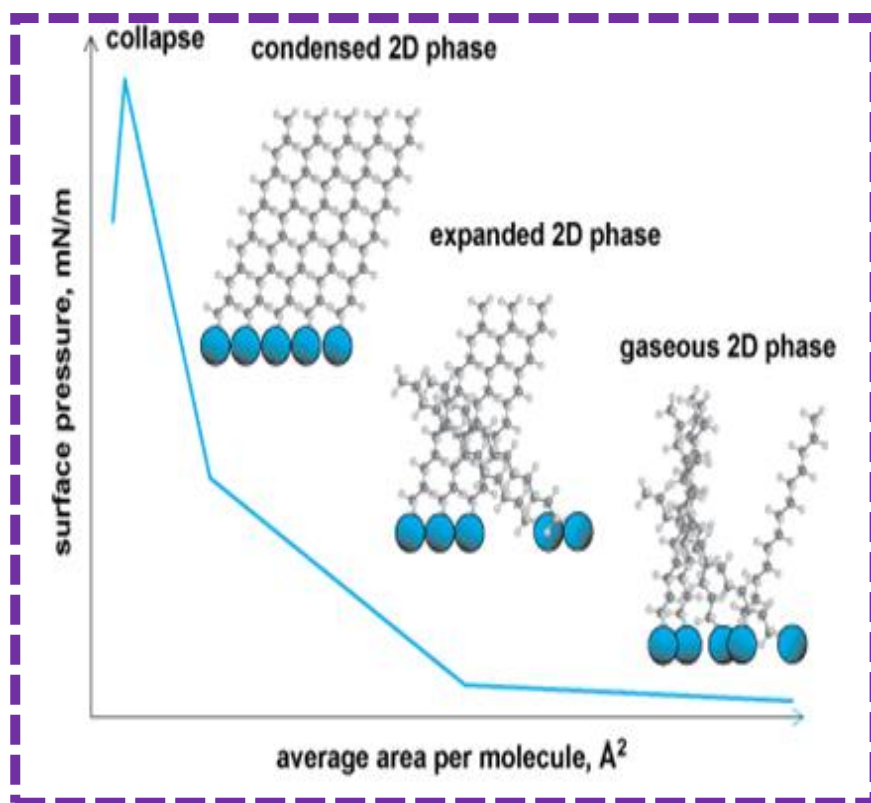


Figure 1.7: Schematic view of molecular arrangement of surface pressure – area isotherm [89].

1.8 Transfer of monomolecular films onto solid substrates

Ordered organic films with a thickness of molecular dimension assembled on appropriate solid surface have attracted considerable attention over the last few decades. The LB method of preparation of ordered monomolecular films onto solid support is based on the transfer of Langmuir monolayers. In this case the Langmuir film formed at the air water interface can be transferred by the vertical dipping, or by the horizontal touching method. These two deposition techniques for the preparation of ordered monomolecular films onto a solid support are:

(a) Langmuir-Blodgett (LB) technique

(b) Langmuir-Schaefer (LS) technique

1.8.1. Langmuir – Blodgett technique

Monolayer is vertically transferred off the water subphase and onto the solid substrate. This was first demonstrated by Blodgett and Langmuir. In this vertical deposition (VD) technique, the monomolecular film is deposited onto a solid substrate by the displacement of a vertical plate and keeping the surface pressure constant. The monolayer can be transferred onto hydrophilic or hydrophobic solid substrate. For the hydrophilic or hydrophobic substrates, the transfer takes place during the upward or downward motion of the substrate respectively (Figure 1.8).

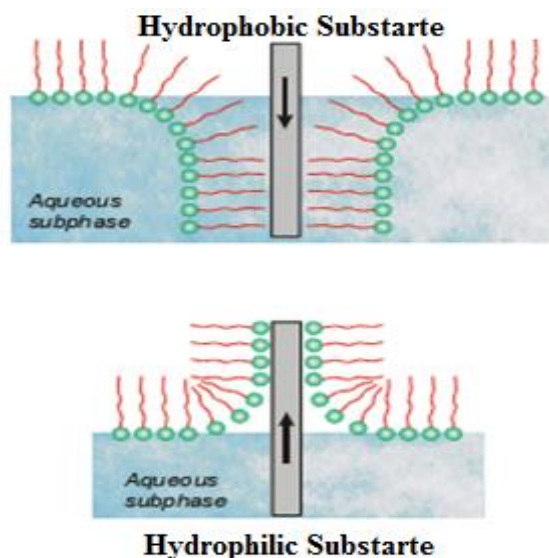


Figure1.8: Scheme of the LB deposition process on hydrophilic and hydrophobic substrates [90].

The amount of monolayer material deposited to substrate is measured in terms of Transfer Ratio (TR).

$$TR = \frac{\text{Area of monolayer removed from subphase}}{\text{Area of substrate immersed in water}}$$

For an ideal transfer the TR is equal to 1. Nature of depositing materials decides the time interval between consecutive layers. By successive up and down strokes of substrates, multilayers of desired thickness can be achieved.

1.8.2 Modes of Langmuir-Blodgett Deposition

There are three modes of Langmuir-Blodgett (LB) deposition X, Y and Z mode. The most common mode of depositing multilayers is Y-type mode. In Y-type deposition both up and down movements of substrate take place. In X-type films are deposited with only up movements of substrate. In Z-type deposition only down strokes are given to substrate to deposit multilayers. Figure 1.9 shows Y, X, and Z- modes of deposition of LB multilayers. Sometimes intermediate structures are also seen in case LB multilayers, they are termed as XY-type multilayers.

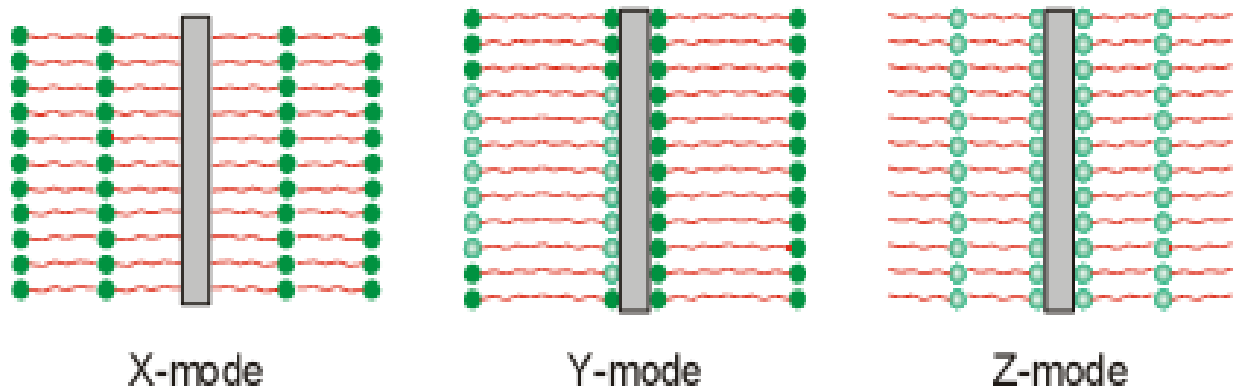


Figure1.9: Structures of multilayers in different modes of deposition of Langmuir Blodgett films [90].

1.8.3 Langmuir – Schaefer Technique

Horizontal lifting of Langmuir monolayer is done from air-water interface to air-solid interface (on substrate) in Langmuir-Schaefer method, introduced by Langmuir and Schaefer in 1938 [91]. In the horizontal touching technique, a solid substrate is placed horizontally on the monolayer. The hydrophobic tails of amphiphilic molecules get attached to a hydrophobic substrate and later with the lifting of the substrate, the monolayer is transferred onto it. Figure 1.10 presents schematic illustration of the Langmuir-Schaefer method.

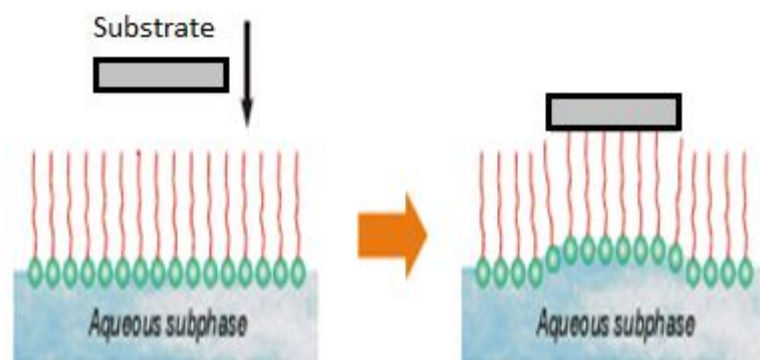


Figure 1.10: The Langmuir-Schaefer method of transfer.

1.9 Parameters affecting LB Film

The significant parameters of the deposition and growth of films are: the control of temperature, concentration, pH, nature of solvent, amphiphilic character of depositing molecules (head, end, functional groups, chain length), transfer process (deposition rate, constant surface pressure, up-down), type and nature of the solid substrate chosen for deposition.

1.10 Advantages of LB Technique

Langmuir-Blodgett technique has many advantages over the other thin film depositing techniques like Spin casting process, Physical Vapour Deposition (PVD), Sputtering, Chemical Vapour Deposition (CVD).

A large number of materials can be deposited by using LB technique at molecular dimensions. The interspacing of molecules forming monolayers can be controlled by changing compression

parameters. In spin casting process a thick film is formed with no specific direction, while with LB technique, ultrathin films are formed with dipping direction. Spin casting is, no doubt, a good deposition technique for organic molecules, but film thickness is relatively high as compared with LB films. This technique is usually used for bottom up assembly in nanotechnology and functional materials applications at room temperature. In Langmuir films, the interactions between hydrophobic and hydrophilic moieties determine the molecular orientation. Materials can be synthesized almost without any limitations with desired functionality. In physical vapour deposition chances of film contamination are very high, due to high temperature. In case of LB, uniform films are deposited at room temperature. In sputtering discharge near the electrodes result in lowering the rate of deposition. In chemical vapour depositing, rate of chemical reaction decides rate of deposition, while in LB speed of substrate decide rate of deposition.

The organization of the nanostructures with LB technique is a representative of bottom-up approach of nanotechnology and put up almost any nanoscale material into the hierarchically organized pattern for microelectronics technology [75].

1.11 Limitations of LB Technique

For LB film deposition substrate should be very smooth. Drying time is required after each layer so the process is slow to fabricate thick films. Mechanical and Chemical stability is poor. Any contamination lowers the surface tension of water so cleanliness is a must. These films have limited resistivity to high temperatures.

1.12 Applications of LB Films.

The LB technique has ability to control over the molecular structure of the films, so thin layers can be deposited for sensor to improve their sensitivity because as the layer thickness reduces the sensitivity enhances [92]. Moreover, the use of ultrathin polymer films in sensors have many advantages such as the wide choice of polymeric systems, dopants in conducting polymers, better sensing performance as compared to that of bulk material etc. [93]. LB Films of conducting polymers are of great interest because of their biocompatibility, their possibility of miniaturization [94], and their use in fabrication of biosensors at the molecular level [95-97].

Several research groups investigated physical aspects of PANi thin films deposited by Langmuir-Blodgett technique, but not much interest has been given to understand the interfacial properties of PANi and PANi-metal oxide nano-composites. The nanoscale arrangement of conductive PANi-metal oxide molecules can result in enhancement of properties. In addition to the fabrication of nanomaterials and uses in the molecular electronics, fundamental processes such as charge transfer mechanisms can be investigated at the molecular level.

Efficient combination of sensors made from Langmuir-Blodgett films of conducting polymers is reported in the literature, but its interfacial, electrical and optical properties still need to be understood to enhance their application in molecular level electronic devices.

The ultra thin LB films can be used for the investigations of single molecular electronic properties by addressing a single molecule on the surface and using either scanning tunneling microscopy or conductive atomic force microscopy.

In this thesis work, the LB technique is used to prepare organized organic –inorganic hybrid systems containing conducting polymer, PANi and metal oxide nano-composite. The structure of the LB system and the electronic and optical properties of PANi within the organized film have been characterized. The nano-composite systems are prepared and their behaviors have been examined by LB thin film technique. By providing molecular leveling ordering to nano-composite system, a new way is opened for many device applications

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CHAPTER 2

Experimental Techniques and Materials Used

Overview

This Chapter includes the experimental techniques, materials and methodology of preparation and characterization of polymer-metal oxide nano-composite systems and their LB films.

Experimental set up and methodology used for depositing thin films by Langmuir-Blodgett method has been explained. The experimental techniques like, UV–visible (UV-VIS) Spectroscopy, Fourier transfer infrared (FTIR) Spectroscopy and X-ray Diffraction (XRD), employed to examine the nano-composites and their Langmuir-Blodgett films have been reviewed. The imaging method for atomic force microscopy (AFM) in contact as well as in non-contact mode for topographical imaging of films, transferred onto a solid support, has also been explained. Experimental details of the setup used for conductive AFM, which provides local I-V characteristics and conductive data imaging are also a part of this chapter. Materials used and synthesis of nano-composites are discussed along with their scheme of reaction mechanisms. A summary of the methodology is given at the end.

2.1 Experimental Setup of Langmuir- Blodgett Deposition Technique

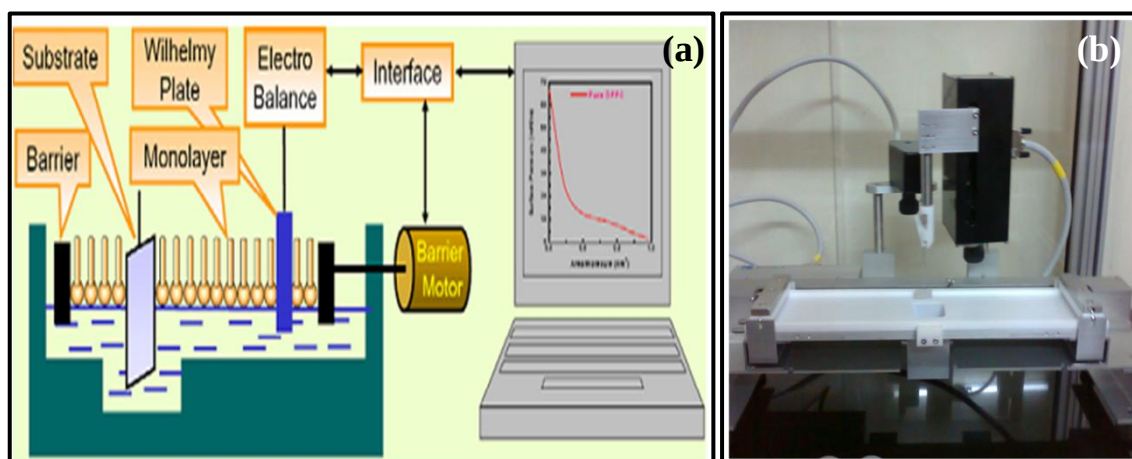


Figure 2.1: (a) Block diagram [1] and (b) Experimental set for Langmuir-Blodgett deposition.

The equipment from KSV-NIMA, Finland was utilized to carry out experiments. This instrument is a single mini trough (160 ml without dipping well) system made up of solid, cast-moulded PTFE (Teflon) with integrated dipping well and aluminium base plate in which there is built-in water piping for temperature control of the subphase (Figure 2.1). Surface area of film is regulated by compressing the monolayer using two moveable barriers, made up of delrin (Polyoxymethylene). Delrin barriers are hydrophilic to prevent leakage under the barrier during compression. The platinum Wilhelmy plate having dimensions (38mm×19.62mm×10mm) was used for the surface pressure measurements with a precision of 0.1mN m^{-1} [2, 3]. Film pressure measuring system (Wilhelmy plate) works on the principle that the sensor connected to the feedback system for surface pressure control. The Wilhelmy plate measurements give surface pressure – mean molecular area per molecule isotherms that show phase transition-like behaviour of the LB films. The deposition of films onto a solid substrate is done by holding substrate into dipper clip, and then dipper is moved vertically through the floating Langmuir monolayer at the air-water interface. The movements of both the dipper and the barrier are done by a servo controlled DC motors, whose speeds can be controlled precisely.

2.1.1. Surface potential measurement

Surface potential was measured using KSV NIMA Surface Potential Sensor (KN 0001) which includes, measuring head, electrode plate and separate stand with height adjustment (Figure 2.2). The Surface Potential Sensor (SPOT) has plug-and-play function with the KSV NIMA Interface Unit and LB Software. KSV SPOT is a computer controlled surface potential measuring instrument. It is a non-contact and non-destructive measurement device based on vibrating plate capacitor method. KSV SPOT has a high accuracy, minimal drift and high reproducibility, which guarantee a high sensitivity and stability. The KSV NIMA surface potential sensor has a precision of $\pm 1\text{mV}$. While the LB software measures the surface pressure at the air-water interface, the surface potential sensor measures the potential difference above and below the film. Variations in the surface pressure are detected only after the formation of a close packed monolayer.

Surface potential measurements are used as an additional source of information about the arrangement of molecules on the water surface. The monolayer surface potential ΔV is defined as the difference between the potential of a clean subphase and a monolayer-covered subphase. The vibrating plate capacitor technique used to measure the surface potential is also known as the Kelvin vibrating electrode method. The difference of potential between two electrodes, one placed in the aqueous subphase and the other in the air above the monolayer surface; is measured in this technique. The electrode moves in the air with respect to the water surface. Due to its vibration, the air gap capacitance changes leading to a flow of current in the external circuit whose magnitude proportional to the difference of potential across the gap. Null method is generally applied, in which the current is nullified using an external bias until the potential difference between the electrodes is zero. The bias voltage gives the potential difference known as the surface potential [4-6]. Figure 2.3 shows the scheme of the surface potential measurements by the vibrating plate method. The surface potential ΔV is described by the Helmholtz formula [7],

$$\Delta V = \mu_{\perp} / A \epsilon_r \epsilon_0 \quad (1)$$

Where A is average molecular area, ϵ_0 is the electric permittivity of vacuum, ϵ_r is the relative electric permittivity of the monolayer, and $\mu_{\perp}$ is the vertical component of the dipole moment defined as $\mu_{\perp} = \mu \cos\theta$ (where θ is the angle between the surface normal and the dipole axis). The surface potential is measured as a function of the area per

molecule, giving the ΔV -A isotherm. Surface potential provides important information on the properties of monomolecular films, in particular, about the orientation of the molecules at the interface during compression.

The whole instrument set-up is placed in an acrylic glass cabinet (CABI S) to avoid air streams and dust deposition and to keep the temperature fixed at $23.0 \pm 0.1^\circ\text{C}$. The temperature was measured using a probe (KN0054), which can be immersed in Langmuir trough from one side and the other side having a wire, connected to the interface unit of KSV NIMA (Figure 2.4). The whole LB film deposition system is computerized through interface unit, which displays barrier position (mm min^{-1}) and surface pressure, (mN m^{-1}) throughout the experiment. A pH measuring probe (Figure 2.5) for KSV NIMA System (KN 0011) was also attached through interface [8-10].

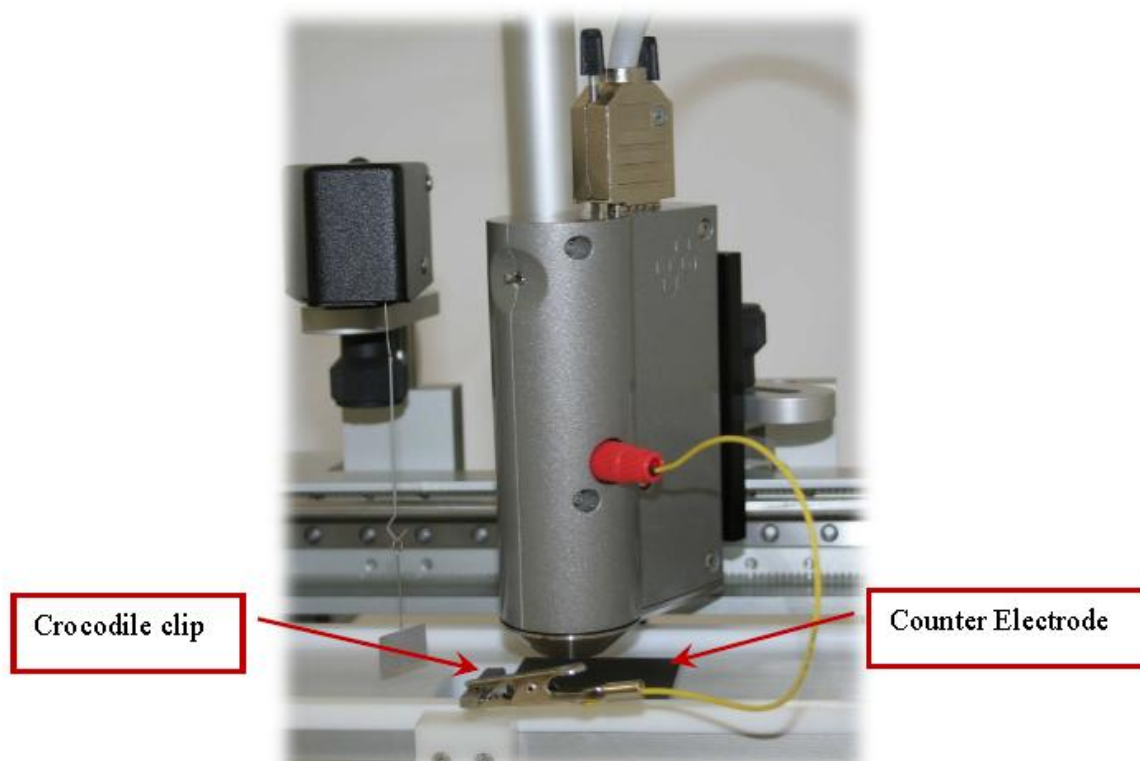


Figure 2.2: Experimental setup for surface potential sensor (SPOT).

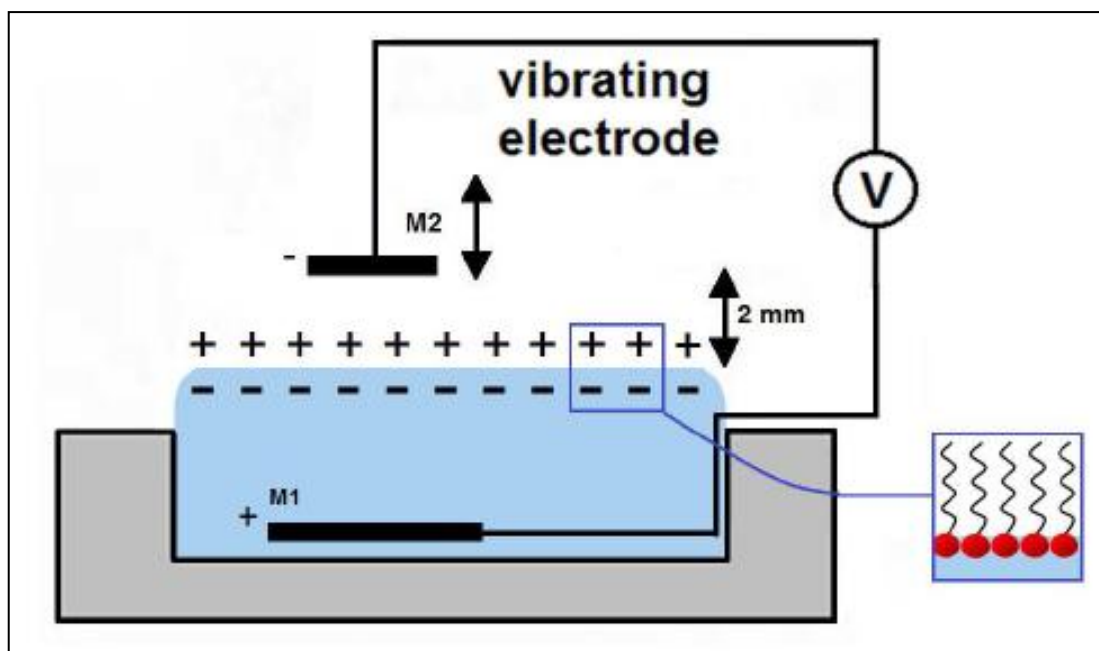


Figure 2.3: Scheme of the surface potential measurement by the Kelvin vibrating electrode method [6].

A computer controlled bath/circulator Julabo F12-MA (KN 0008) is used for setting and monitoring the temperature of the subphase, which is connected to the trough with special connectors (Figure 2.6). These connectors have valves in both parts, so the connection can be opened without any leakage. Temperature ranges from -20°C to $+200^{\circ}\text{C}$ (Stability 0.02°C)

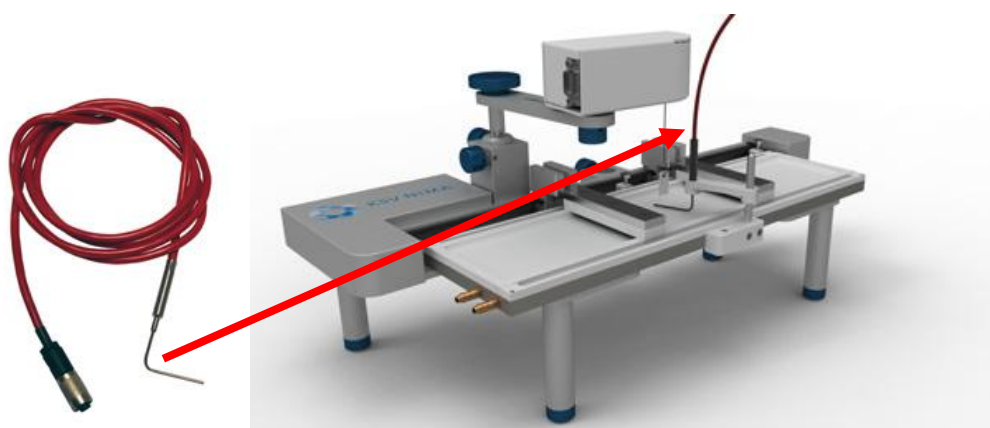


Figure 2.4: Temperature measuring probe.



Figure 2.5: pH measuring probe.



Figure 2.6: Picture of bath/circulator.

2.1.2 Trough Cleaning and Subphase:

Proper cleaning of trough is very essential to study molecular interactions at the air-water interface. Trough is cleaned with ethanol [Merck (AR)] and followed by rinsing with deionized water. The proper cleanliness of the trough is ensured by draining the Millipore water (Direct Q₃) and completely drying the surface. The trough was thoroughly cleaned, before starting each experiment. The subphase most commonly used for the study of monolayers is ultra pure water obtained from Milli-Q ultra pure water purification system. The resistivity of the water was 18.2 MΩ.cm. The pH of the water is ~6.0. In order to check the cleanliness of the trough, a test isotherm was performed. The trough was filled with type 3 deionized water and the Wilhelmy plate (cleaned by dipping in ethanol) was lowered until it touched the surface of the water. Once the plate stabilizes, the pressure reading is made zero and the barriers are closed at a rate of 35 mm/min [11]. If surface pressure value remains below 1 mN/m during the compression, the trough is considered to be clean and ready for use.

2.1.3 Solution Preparation and spreading on Subphase:

Solution (mg ml⁻¹) of the desired material is prepared using water insoluble solvent whose density is higher than water such as NMP. The polymer has good solubility in NMP. Solutions are ultrasonicated for sufficient time to ensure proper dissolution. Solutions are kept in an airtight container so that their concentrations remain unaltered.

The solution is spread on the water surface by Hamilton micro syringe. Small drops at a distance of a few millimetres above the subphase, are placed uniformly. Before starting the compression process with barriers, solvent settling time is given in each experiment.

2.1.4 Cleaning of Substrates and Deposition:

Indium tin oxide (ITO) coated conducting glass and quartz substrates were used for thin film deposition. ITO-coated glass was cleaned with acetone, then ultrasonicated for about half an hour in 10% aqueous solution of sodium hydroxide, and rinsed in deionized water for about 10 minutes [12]. The substrate was dried and clamped to the dipper. LB films were deposited on substrates using the vertical dipping method at the rate of 0.5 mm min⁻¹ downstroke and 2.0 mm min⁻¹ upstroke, respectively. The depositions were made at a

constant pressure of 10mNm^{-1} , and started from above the surface, after 10 min of stabilization. The deposited film was dried for about 5 min and then placed in a vacuum desiccator to ensure a moisture free environment. Quartz substrate was washed with acetone, followed by deionized water and the process was repeated to deposit thin films.

2.2 Fourier Transform Infra-red Spectroscopy

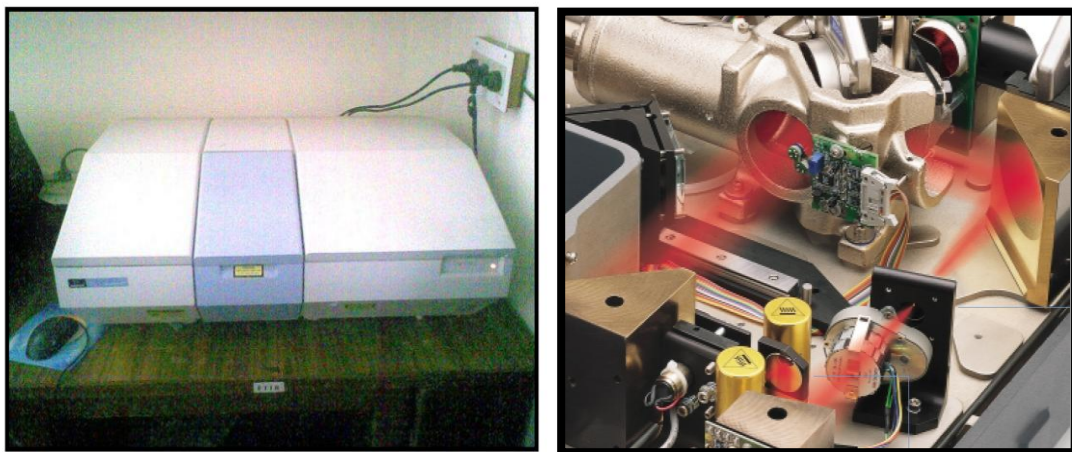


Figure 2.7: FTIR Spectrometer present at laboratory outside view and inside view.

FTIR measurements are carried out at room temperature by the spectroscope (BX-II, Perkin Elmer) having resolution 4cm^{-1} and scan range $400\text{-}4000\text{ cm}^{-1}$ (figure 2.7). Sixteen scans are taken to ensure accuracy of results for each film.

FTIR spectroscopy works on the principle of selective absorption shown by chemical substances in the infrared region, which gives rise to closely packed absorption bands known as infrared (IR) absorption spectrum, which may extend over a wide range of wavelengths. These bands are the signatures of characteristic functional groups and bonds present in the chemical substance. The IR spectrum of a chemical substance thus occupies an important place as an investigation and is known as fingerprint of the chemical substance for its identification. Band position in infrared spectrum may be expressed by wave number ν for convenience, whose unit is cm^{-1} . The relation between velocity c , wavelength λ and frequency ν is as follows;

$$\nu = c/\lambda \text{ or } \nu/c = 1/\lambda \quad (2)$$

When LB film is placed on sample holding stage, IR radiation is passed through film deposited on a glass substrate. Some of the infrared radiation is absorbed by the film and

the rest is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the film.

So, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material present in the film. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. The normal instrument layout of FTIR is shown in figure 2.8. The source emits infrared energy which is passed through an aperture, to get desired and controlled amount of energy.

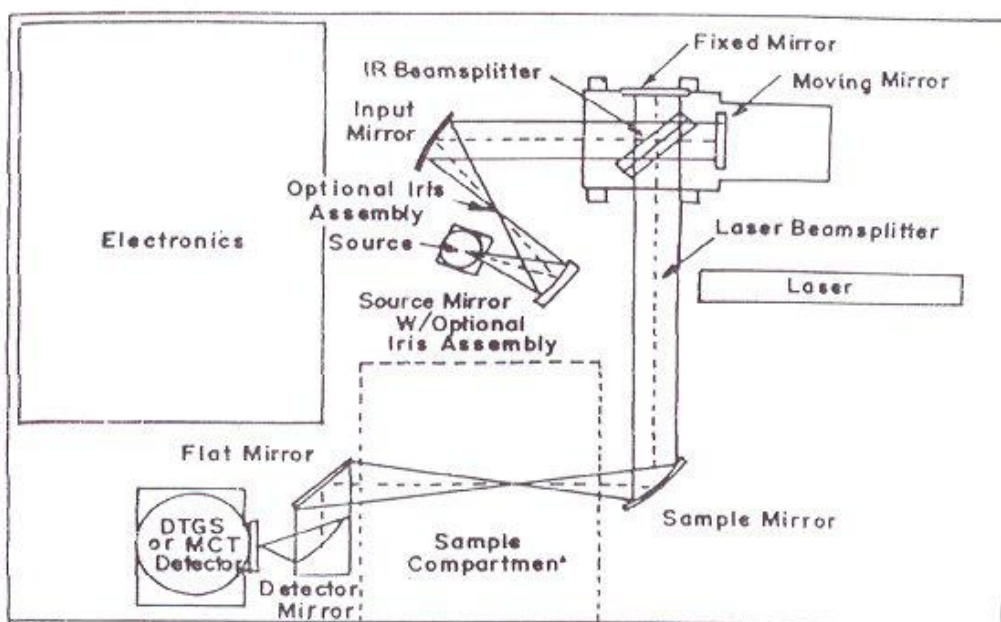


Figure 2.8: Simple Spectrometer Layout of FTIR [13].

This controlled beam of energy is passed through the interferometer before sending to sample compartment. The optical path of the beam is controlled by its reflection from the mirror. When the beam falls on film mounted on sample holder, it gets transmitted from the surface of the sample. The specific amount of frequency is absorbed by the sample. The beam passes through the detector for final measurements after getting reflections from the beam. Detectors are specially designed to measure interferogram. This measured signal is again converted into digital signal before sending to the computer. In the computer Fourier transformation of the signal is takes place.

2.3 X-Ray Diffraction Study

I have used Philips XPERT–PRO MPD X-Ray Spectrometer for XRD studies. Laboratory view of XRD is shown in figure 2.9. X-ray diffraction is the most widespread technique

for determining the phase identification, crystal structure and lattice parameter of the crystalline solids. A typical XRD instrumentation consist of four main components such as X-ray source, specimen stage, receiving optics and X-Ray detector as shown in figure 2.10.



Figure 2.9: Laboratory view of X-Ray Diffraction spectrometer.

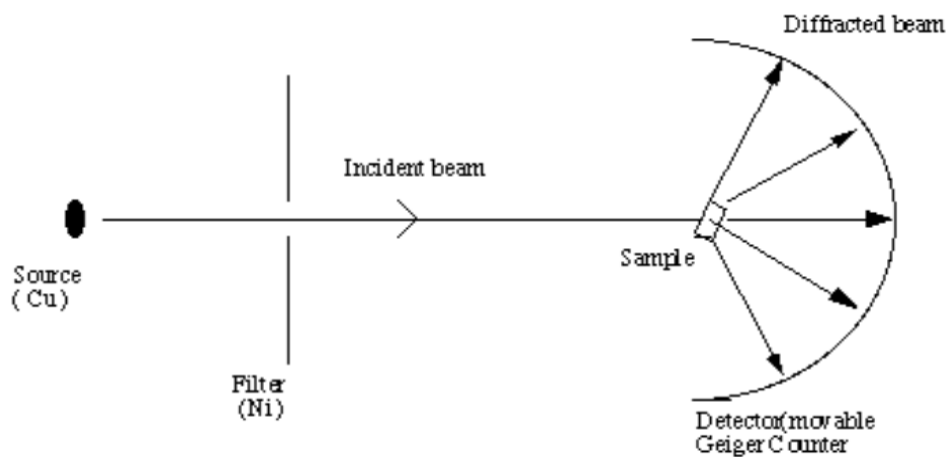


Figure 2.10: Schematic view of Optical axis of X-Ray Diffraction spectrometer [14].

The source and the detector with their associated optics lie on the circumference of the focusing circle and the sample stage lies at the center of the circle. The angle between the plane of the specimen and the X-ray source is θ , known as Bragg's angle and the angle between the projection of X-rays and the detector is 2θ [15, 16]. The X-ray diffraction experiment gives plot of the intensity as a function of the diffracted angle θ . Diffraction experiments give information of peak position, peak intensity and peak shape.

2.4 Ultraviolet-Visible Absorption Spectroscopy

Ultraviolet-Visible absorption spectroscopy is the measurement of the attenuation of the beam of light after it passes through a sample or after getting reflected from a sample surface. UV-Vis includes measurements of transmittance, absorption and reflection in the UV, visible and near Infra Red regions [17]. The absorption of UV radiation organic compounds in the visible and ultraviolet region involves transition of electrons in σ , π and n-orbitals from the ground state to the higher energy state. These higher energy states are described by molecular orbitals that are vacant in the ground state and are commonly called anti bonding orbitals. The anti bonding orbitals associated with σ bond is called the σ^* orbital, and that associated with π bond is called the π^* orbital. The electronic transitions that are involved in the UV and visible regions are of various types viz; σ to σ^* , n to π^* and π to π^* . Transitions to antibonding π^* orbitals are associated only with unsaturated centres in the molecule. Compounds containing isolated double bond absorb in the range 162-190nm, whilst conjugated molecules (those containing single and double bond) absorb above 210nm. Extension of conjugated systems intensifies the absorption peaks and shifts it further to higher wavelengths, towards the visible spectrum. Absorption spectroscopy region is also called electronic spectroscopy. Figure 2.11 depicts various electronic excitations occurring in organic molecules. Of the six transitions outlined, only the two with the lowest energy (leftmost, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. The energetically favored electron transition will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called in excited state [18].

The components of a typical spectrometer are shown in Figure 2.12. The instrument functioning involves the separation of a beam of light from a visible or UV light source into its component wavelengths by a prism or diffraction grating. Each monochromatic beam in turn is split into two equal intensity beams by a half-mirrored device. One of the

beams, the sample beam, passes through cuvette containing the compound being studied dissolved in a solvent. The other beam, the reference beam, passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I_0 . The intensity of the sample beam is defined as I . The ultraviolet (UV) region scanned is normally from 200-400 nm, and the visible portion is from 400-800 nm.

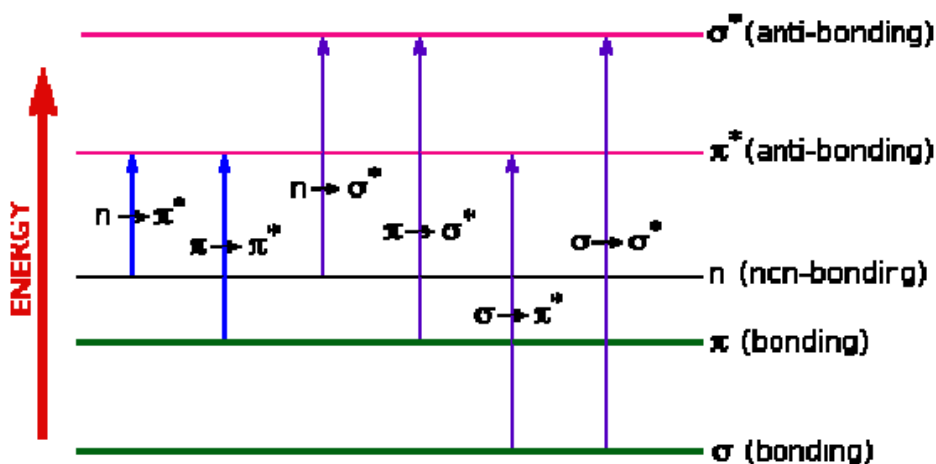


Figure 2.11: Energy Level Diagram of electronic excitation in organic molecules [19].

As the sample compound absorbs light, so the value of ' I ' is less than ' I_0 '. The difference is plotted against wavelength. Absorption is either represented as transmittance ($T = I/I_0$) or absorbance ($A = \log I_0/I$). Generally, absorbance is displayed along the vertical axis with a range from 0 (100% transmittance) to 2 (1% transmittance). The wavelength corresponding to maximum absorbance is a characteristic value, denoted as $\lambda_{\max}$ [20].

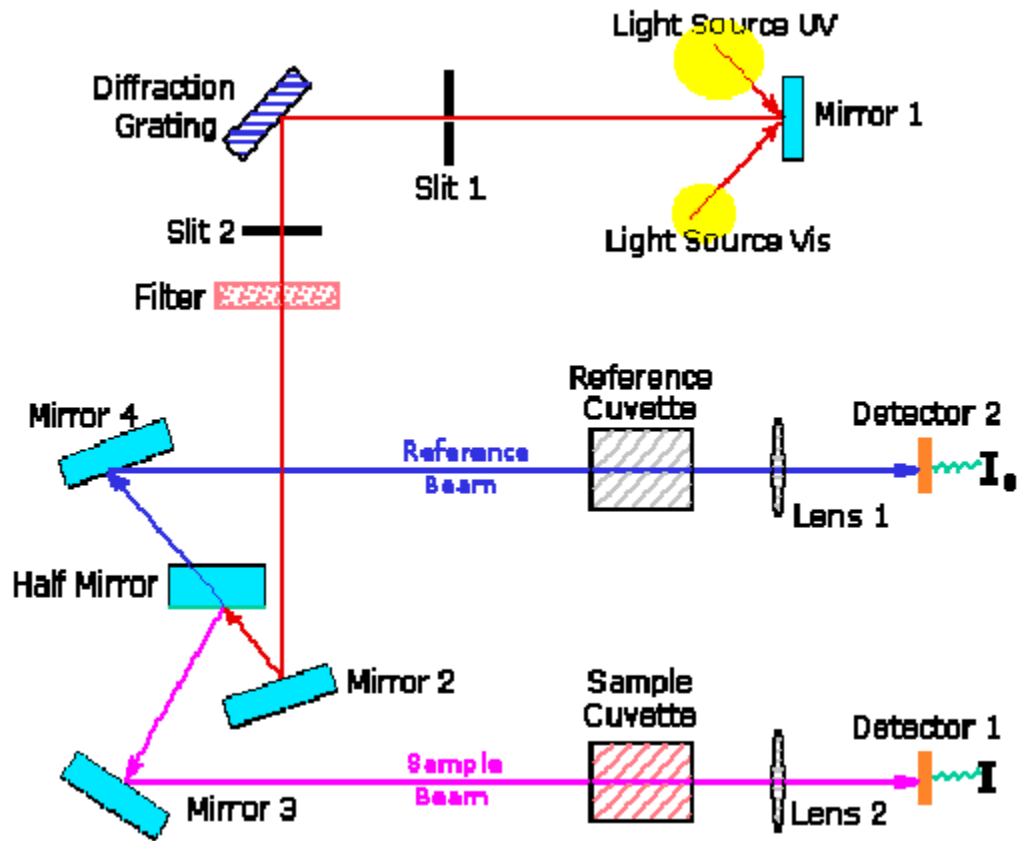


Figure 2.12: Block diagram of Ultraviolet-Visible Spectrometer [21].

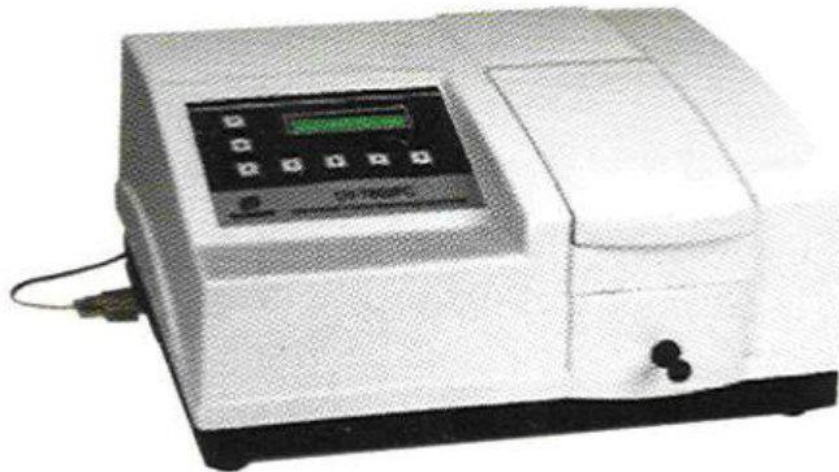


Fig. 2.13: UV-Vis spectrophotometer.

Samples are placed in transparent rectangular cells with an internal width of 1 cm, known as cuvette. Quartz substrates are used for LB film fabrication for UV-Vis spectroscopy because these are transparent throughout the UV, visible and near infrared regions.

2.5 Atomic Force Microscopy



Figure 2.14: Laboratory view of Atomic Force Microscope.

Atomic force microscopy (AFM) (Solver-NEXT NT-MDT; Zelenograd, Moscow, Russia) is used for topographical investigations of the thin films as shown in figure 2.14. For non-contact mode AFM imaging (scan rate 1 Hz) Silicon nitride (NT-MDT), probe with tip curvature radius 6 nm attached to a cantilever (resonance frequency; 87-230 kHz, typical force constant 5.1Nm^{-1}) is used. The topographical data is sampled in a grid of 512×512 points. A properly cleaned substrate is scanned under AFM to check its root mean square roughness. If roughness $< 1\text{nm}$ is observed then smoothness of the substrate and its sustainability for monolayer deposition is ensured. Contact mode AFM is done by using conductive Pt-coated silicon AFM tip (NT-MDT), attached to a cantilever having resonance frequency 4-17 k Hz and force constant 0.03Nm^{-1} . AFM images are processed with the NOVA P9 Software (Image Analysis 2.1.0.800) which is used to determine the 3-D view and height profiles also.

A schematic view of an atomic force microscope is shown in figure 2.15. Tip is attached at the edge of the cantilever. The head of the tip is usually coated with a reflecting material like Silicon nitride (SiN). When laser light falls, it gets illuminated. The reflected light from tip surface is collected on a photodiode. The sample is mounted on a piezo scanner. It can move in all the X, Y and Z directions.

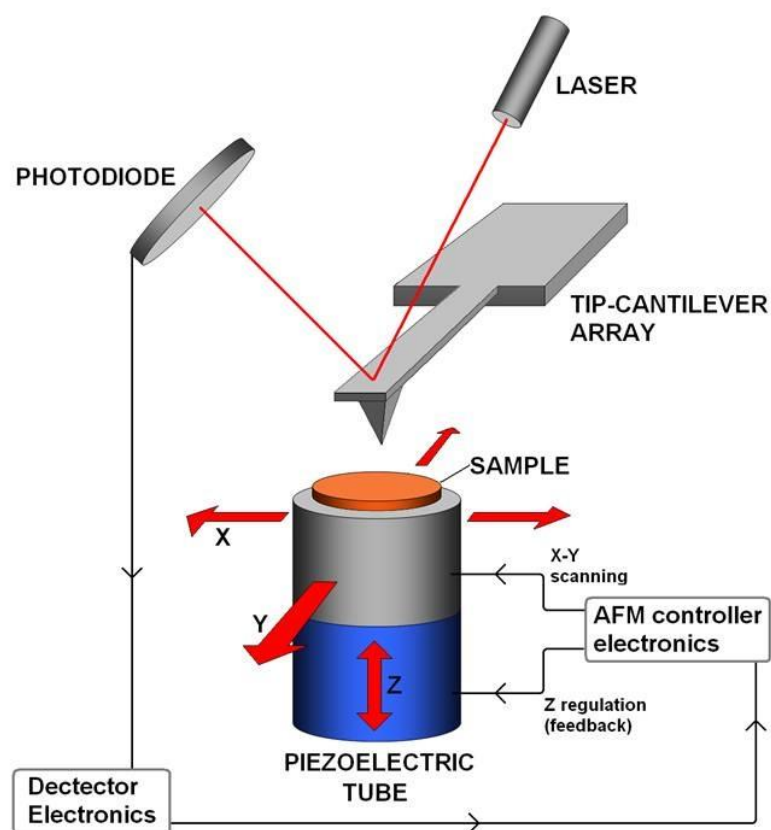


Figure 2.15: Scheme of atomic force microscope (AFM) operation [22].

The deflection of tip occurs due to its interaction with the sample, which is monitored by measuring changes of light intensity on the photodiode. There are a number of modes of operation of the AFM. Langmuir-Blodgett films are of soft organic material. They are analysed under the non-contact mode of scanning [23, 24]. In non-contact mode AFM, phase detection microscopy is used to monitor phase lag between the signal driving the cantilever oscillation and the output signal of cantilever oscillation.

In this mode oscillations are produced in the cantilever by using an electrical oscillator [25]. When the cantilever is away from the sample, free oscillations occur due to non interaction zone. When it approaches the sample surface, the tip is attracted towards the sample via Vander wall forces, thus reducing the amplitude of cantilever oscillation. The amplitude of the oscillations can be kept constant at a fixed cantilever-sample distance. The sample surface is scanned at constant amplitude using a feedback loop as shown in figure 2.15.

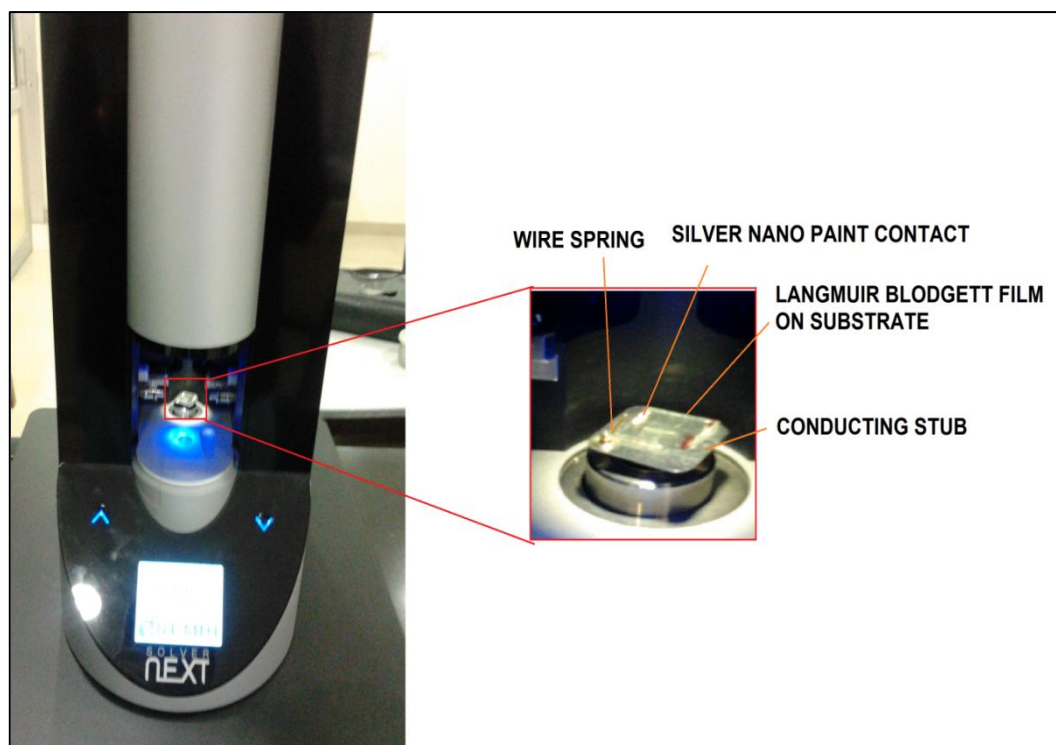


Figure 2.16: Experimental setup for conductive AFM

In C-AFM, conducting probe is used to scan the sample in contact mode, while a DC bias is applied between the conducting tip and the silver nanopaint contact on the ITO-coated glass (Figure 2.16). For current mapping, current was recorded at constant voltage as a function of position; for current–voltage (I–V) characterization, the current was also recorded as a function of voltage at a specified sample position [26]. Unlike other scanning probe-based techniques, C-AFM enables simultaneous and independent acquisition of topography and current maps of samples at a fixed voltage, which helps in distinguishing highly and poorly conducting regions [27–29].

2.6 Materials Used

Aniline (LR for synthesis, purity 99%) and acetone (Guaranteed grade, purity 99.5%) were purchased from M/S Loba Chemie. Ammonium persulfate (APS) ($(\text{NH}_4)_2\text{S}_2\text{O}_8$ (AR, purity 98.5%), N-methylpyrrolidone (NMP) (LR, purity 99.5%) and TiO_2 (25 nm) were purchased from Degussa P-25. Hydrochloric acid, sodium hydroxide (AR) purchased from M/S S. D. Fine-chemicals and Ethanol (AR, purity 99.9%) purchased from Merck were used without further purification. We used TiO_2 (25 nm) from Degussa P-25 and zinc oxide (ZnO) nanopowder (<50 nm, purity 97%) from Sigma–Aldrich. Milli-Q

filtered (Direct Q3) deionised and ultrapure water (Resistivity~18.2 MΩ cm) was used for synthesis of nano-composites and for preparing the subphase.

2.7 Preparation of PANi–TiO₂ Hybrid Nano-composites and PANi

PANi–TiO₂ nano-composite systems were prepared by chemical route. Aniline (1.6 ml) was injected for the dispersion of 50 ml of 2M HCl containing TiO₂ powder, under ultrasonic action to avoid the agglomeration of TiO₂ nanoparticles. After 30 min, APS was mixed into this dispersion system with constant stirring and keeping the temperature of the reaction system between 0 and 5°C. The resulting mixture was allowed to react for 10h at room temperature. The precipitated powder was filtered by using Millipore vacuum filter (pore size ~0.22 μm) and washed with deionised water to remove the unreacted aniline monomer. These nano-composites with different concentration of TiO₂ were doped by treating with 1L of 1M HCl solution. PANi was prepared by similar procedure in the absence of TiO₂ [30]. The final compound was dried in vacuum at 40°C for 24h. The molar ratios of aniline to HCl and to APS for either PANi or PANi–TiO₂ nano-composites were kept at 1 : 0.5 and 1 : 1, respectively [12].

2.8 Preparation of PANi–ZnO Nano-composites

To prepare PANi–ZnO nano-composites, 1.6 ml aniline was injected into 50 ml of 2 M HCl containing ZnO nanopowder to form dispersion. The procedure was conducted under the action of ultrasound to prevent agglomeration of the ZnO nanoparticles. After approximately 30min, ammonium persulfate (APS) was added dropwise to the dispersion, with constant stirring, while keeping the temperature of the reaction between 0 and 5°C. The resulting mixture was left to react for 10h at room temperature. The precipitate obtained was isolated by filtration through a Millipore vacuum filter (pore size~0.22 μm) and washed with deionised water to remove unreacted aniline monomer. This powder, containing ZnO, was doped by treatment with 1 litre 1 M HCl solution. The final products were dried under vacuum at 40°C for 24 h. The molar ratios of aniline to HCl and APS for pure PANi and PANi–ZnO nano-composites were 1:0.5 and 1:1, respectively [31, 32].

2.9 Methodology

The experiment consists of three distinct steps

1. Preparation and characterization of the nano-composites.

2. Preparation and characterization of the nano-composite monolayers (Langmuir films) at the water-air interface
3. Fabrication and characterization of the LB films on various solid supports.
Characterization of ultrathin LB films.

A concise view of methodology is presented in form of flow chart in Figure 2.17.

To prepare LB films, solutions of polymer-metal oxide nano-composite materials are prepared in NMP by ultra sonicating it. Subphase is prepared at required pH and temperature. A clear solution obtained by sonication is spread on subphase by using micro syringe [33].

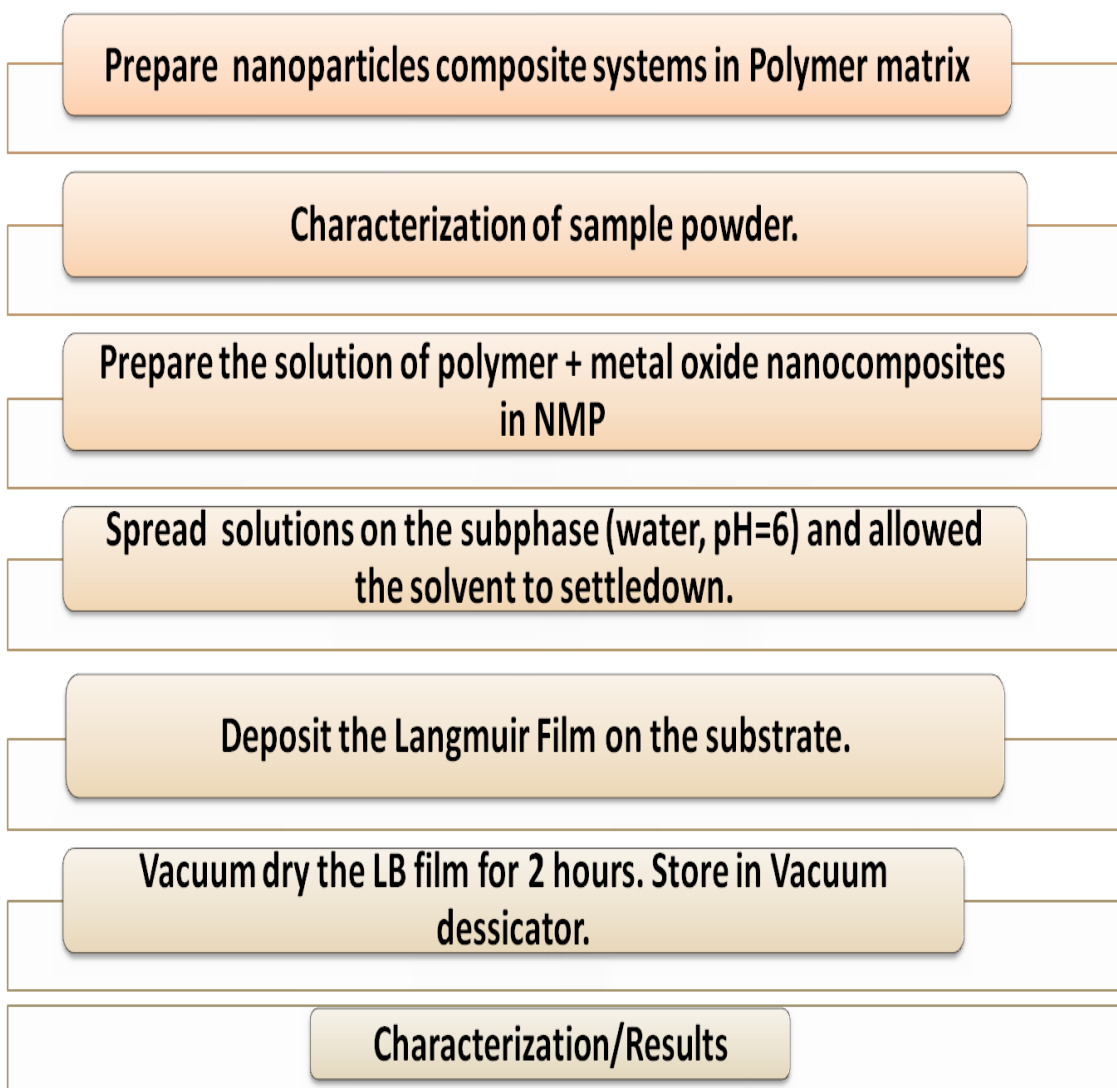


Figure 2.17: Flow Chart showing Langmuir-Blodgett films preparation and characterization.

Dipper motor is allowed to take substrate through air-water interface. Then barriers are compressed uniformly at very slow rate. Isotherm is recorded with decrease in trough surface area. Films are deposited on solid substrates; choice of substrate is dependent upon type of characterization. The deposited films are characterized for electrical, optical, structural, thermal and morphological properties.

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CHAPTER 3

Optical, Thermal and Electrical Investigations of Langmuir-Blodgett Thin Films of Polyaniline (PANI): Optimization of Various Physical Parameters

Overview

Langmuir-Blodgett (LB) films of synthesized polyaniline (PANI) has been deposited onto suitable solid substrates after optimization of various physical parameters for growing appropriate Langmuir monolayers at the air–water interface and LB films at air–solid interface. The significant parameters for the deposition and growth of films are discussed briefly.

Surface pressure–area (π -A) isotherms show phase transformations in the monolayer during the compression process. Langmuir–Blodgett films of PANi show that during barrier compression the interaction between molecules in the monolayer was increased, resulting in increased surface pressure. Multiple isotherms indicate that the monolayer of the material can retain its configuration during compression-expansion cycles. Electrical effects in Langmuir monolayers are investigated by surface Potential measurements and dipole moment of Langmuir monolayer of PANi at various temperatures is calculated using Helmholtz equation. Langmuir–Blodgett thin films of PANi were deposited on the quartz and indium tin oxide coated conducting glass substrates. Fourier transfer infrared spectroscopy, UV–visible spectroscopy and X-ray Diffraction study indicates formation of PANi LB Films. The topography of Langmuir–Blodgett films was also characterized by atomic force microscopy with average height profile of 25 nm. Local Current-voltage (I-V) spectroscopy results by C-AFM show semiconducting behaviour of PANi LB film. Conductive data images show almost uniform current distribution through the PANi LB films.

3.1 Introduction

Conducting polymers have emerged as novel electronic materials considering their use in molecular electronic devices. These materials possess the electronic properties of semiconductors as well as the flexible behavior of polymers [1–6]. Amongst the family of conducting polymers, polyaniline (PANI) has special characteristic due to the presence of reactive $-NH-$ groups in a polymer chain, which imparts hydrophilic character to the system, relatively high conductivity, and good chemical stability [7,8].

Polyaniline (PANI) is an extensively studied conducting polymer due to its good tunable conductivity, environmental stability and easy processability [9-12].

Technological applications of polyaniline include gas sensors [13, 14], taste sensor [15], humidity sensor [16], temperature sensor [17], chemical Sensors [18, 19]. Polyaniline is a promising material for applications in many fields, for example in biomolecular electronic devices [20], polyaniline coated fabric based microwave shields [21, 22], EM shielding materials [23, 24], corrosion inhibitors [25]. Free $-OH$ and $-NH_2$ groups in the polymer chain can adhere to other functional groups enabling it to be used as antistatic materials [26]. Nano-composites of polyaniline nanowire with graphene oxide sheets find application in supercapacitors [27] Conductive polyaniline also find applications in x-ray mask making [28].

Langmuir–Blodgett (LB) method offers a fantastic and relatively simple method of producing ultra-thin films, with fine control over film thickness. Density and homogeneity are preserved in the LB films, giving the possibility to create self-assembled multilayers with variable layer compositions. It also facilitates to prepare single molecule thin electronic device from nano- or micro-sized metal rods or particles using this technique. Spin casting is also a good deposition technique for organic molecules but film thickness is relatively high as compared with LB films. This technique is usually used for bottom up assembly in nanotechnology and functional materials applications at room temperature. In Langmuir films, the interactions between hydrophobic and hydrophilic moieties determine the molecular orientation. The required amphiphilicity of PANi is provided by the presence of $-NH-$ groups, benzoid and quinoid rings in a polymer chain. Thus, several research groups made attempts to investigate thin films behavior of conducting polymers using LB technique with PANi getting special attention [29-32], but

not much effort has gone to understand the interfacial and electrical properties ultrathin LB films of PANi. Properties of nanomaterial rely upon the morphology produced, so understanding polyaniline's tendency of forming nanostructures is pivotal for different applications as well as bettering its synthesis.

In this chapter, we have made an attempt to study the organization and orientation of PANi molecules at various temperatures by Langmuir-Blodgett technique. The significant physical parameters like control of temperature, concentration, pH, nature of solvent, molecules (head-, end-, functional groups, chain length), transfer process (up-down speed of substrate, surface pressure), nature of substrate etc. for the deposition and growth of films are optimized.

Surface Pressure- Area (π -A) isotherms, multiple isotherms during compression and expansion cycles of barriers, Fourier Transfer Infrared spectroscopy (FTIR), UV-visible spectroscopy X-Ray diffraction profile (XRD), and Atomic Force microscopy (AFM) and Conductive Atomic Force microscopy (CAFM) image analysis have been carried out to study the structural, thermal, optical and electric properties of LB films.

3.2 PANi Monolayer at Air-water Interface

3.2.1 π -A Isotherm:

The spreading solution of PANi was prepared in N-methylpyrrolidone (NMP) by sonicating the mixture for ten minutes and particle concentration is 0.2 mg/mL. A total of 200 μ L of the solution was spread on the ultrapure Milli-Q₃ (pH=6.00) water subphase contained in trough by using a Hamilton micro syringe. The pH of the subphase is 6 (measured by pH probe). The density of NMP was higher than that of water, so it got settled down at the bottom of subphase leaving behind the material to be deposited, on the water surface [33, 34]. The solvent settled down in about 30 min before the area enclosed by the barriers was reduced at 10 mm min⁻¹ to compress the molecules on the water surface. The stability of the monolayer is monitored by holding the monolayer at the target pressure and noticing the change in mean molecular area with respect to time. When there is no change in the mean molecular area and surface pressure with time, then monolayer is considered stable and ready to transfer on solid substrate.

Figure 3.1 shows a profile of surface pressure (π) as a function of mean molecular area (Mma) of PANi taken at constant compression rate 10 mm min⁻¹ at room temperature. Initially with open barriers, molecules were randomly oriented having negligible

interactions between them. While closing the barriers at a constant speed, compression resulted in various molecular interactions at the air-water interface. The molecules were initially in the gaseous phase (a to b) from lift off area (A_i) $\sim 15.74 \text{ \AA}^2/\text{molecule}$, surface pressure varied from 0.02 to 0.70 mN m^{-1} . Molecules show a plateau region as shown in the π -A isotherm due to the molecular arrangement during the transition from gaseous to condensed phase. At large area per molecule, the molecules remain flat on the subphase surface. As further compressed, the polymeric chain lifts off the water surface [35], resulting in a molecular rearrangement among the molecules. With a further compression of barriers, gradual rise is observed in the surface pressure up to 9.6 mN m^{-1} . Thus, molecules had reached to a condensed phase (b to c) due to their molecular arrangement and ordering at air-water interface with compression of barriers. At this stage, the monolayer was compressed to limiting area (obtained by extrapolating isotherm curve to zero surface pressure), $A_0 \sim 13.49 \text{ \AA}^2$.

Figure 3.2 show π -A isotherm profile of PANi monolayer at various temperatures. Isotherm behavior is not much affected with the variation of temperature. The slight variation in isotherms may be due to the change in surface tension of subphase water with variation of temperature which leads to the chain ordering. Generally, surface tension decreases with rise in temperature due to the reason that cohesive forces decrease with increasing of molecular thermal activity [36].

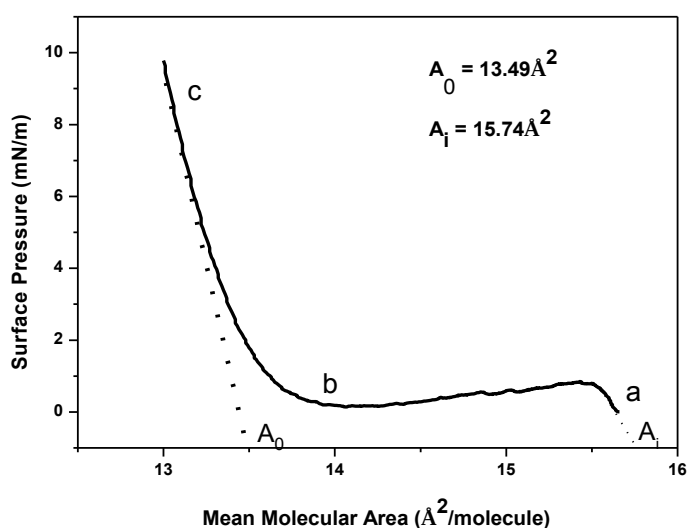


Figure 3.1: π -A isotherm profile of PANi monolayer, particle concentration 0.2 mg/mL in NMP solution, spreading amount 200 μL , and compressed to target pressure 10 mN/m at 10 mm/min.

3.2.2 Hysteresis in π -A Isotherm:

To check the reversibility and stability of the layer formed at the air-water interface, three compression-expansion cycles were performed as shown in figure 3.3. During decompression, the expansion curves show almost similar trends as shown by compression curves.

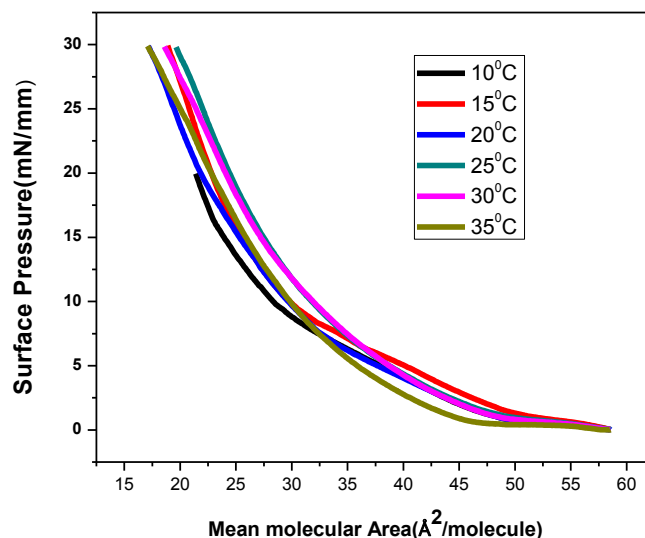


Figure 3.2: π -A isotherm profile of PANi monolayer at various temperatures.

It is found that continuous compression–expansion cycles have negligible hysteresis. It establishes the stability of the monolayer at water surface, which clearly proved that during compressing of barriers none of the molecule had squeezed out from the water surface and hints that molecules retain their orientation and positional order during three cycles.

The substrate was dried and then clamped to the dipper. Langmuir monolayers were transferred on precleaned substrates using the vertical dipping method at 0.5 mm min^{-1} downstroke and 2.0 mm min^{-1} upstroke, respectively. The stable monolayers were successfully transferred to substrates by using Y-type deposition method [37]. The deposited films were dried for about 5 minutes and then placed in vacuum desiccator to ensure moisture free environment.

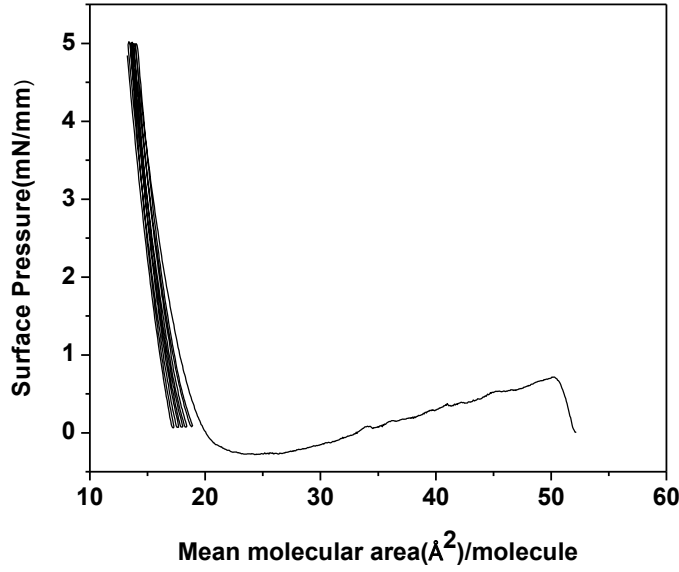


Figure 3.3: Surface pressure as a function of mean molecular area (π -A) compression–expansion cycles.

3.2.3 Electrical Effects in Monolayers:

Surface Potential and Dipole Moments of PANi Langmuir Monolayers at Various Temperatures

The monolayer is formed from polar molecules having a dipole moment, μ . A double layer of charge is formed by the alignment of molecules at the surface giving rise to a volta potential. The change in the volta potential between the clean water and monolayer coated surface is called the surface potential, ΔV (Helmholtz equation)

$$\Delta V = \mu_{\perp} / A \epsilon_r \epsilon_0 \quad (1)$$

where $\mu_{\perp}$ is the apparent dipole moment, which corresponds to the vertical component of the dipole moment of a molecule, and A is the area per molecule. ϵ_r is monolayer's relative electric permittivity, ϵ_0 is the vacuum permittivity ($8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$) and A is the area per molecule. The dipole moment is named as apparent dipole moment because in Helmholtz model the monolayer is considered to have a unity dielectric constant [38, 39].

Surface potential measurement provides information of net dipole moment per molecule and molecular orientation. Being aggregated, molecules tend to orient themselves in energetically adequate position, giving rise to the variation in the surface potential. Dipoles which are present at film will intend to change physical properties in terms of molecular ordering and packing fraction.

Three different regions are usually considered for the surface potential interpretation according to the three-capacitor model of Demchak and Fort [40, 41] (figure 3.4). The first one (μ_1) is due to the dipole orientation of water molecules in the area just under the monolayer. The second one (μ_2) is connected to the regular arrangement of the polar head-groups and the third one is due to the orientation of the C-H bonds in the hydrocarbon chains of the amphiphilic molecules during the monolayer formation i.e. μ_3 arises from the hydrophobic moiety. The relative input of each of regions can be different and it is due to the nature of the molecules forming the monolayer [42, 43].

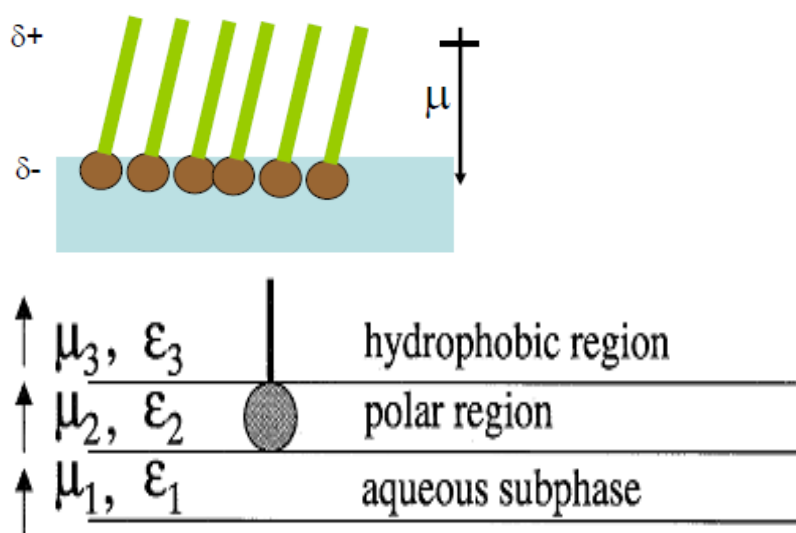


Figure 3.4: Demchak and Fort Model [42].

Fig. 3.5 shows that the surface potential isotherms for PANi recorded as a function of mean molecular area/molecule ($\text{\AA}^2/\text{molecule}$) during compressions. Surface potential (ΔV) and dipole moment (μ) increases with temperature and becomes +ve at room temperature. At 30°C surface potential reaches the high value of 1100mV. The molecular interactions that occur during monolayer compression can be identified by simultaneous recording of surface pressure and surface potential of monolayer at air-water interface. Dipole moment for molecules of Langmuir monolayer has been calculated using Helmholtz's equation and is plotted as shown in Fig. 3.6 for PANi [35].

When pressure is applied, the disordered and loose-packed molecules lying on the subphase are forced to orient and close-packed. This results in a fall of significant area per molecule, values of surface potential varies significantly. In liquid-state and in solid-state the area and surface potential of film molecule undergo smaller changes than in gaseous-state. The $\Delta V - A$ curve falls a little earlier than $\pi - A$ isotherm curve because of the reason that when applied pressure increases and the solid state is about to collapse and spread molecules are more closely packed in the film and surface potential amplitude falls. Positive or negative values of surface potential depend upon the chemical structure of the molecules forming the film [44].

Figure 3.6 shows the variation of the vertical component $\mu_{\perp}$ of the dipole moment of the monolayer with area per molecule under compression of barriers. $\mu_{\perp}$ is calculated from the Helmholtz formula. $\Delta V - A$ isotherms indicate that with the compression by barriers both the tilt angle and the head group conformation of the molecules in the monolayer change simultaneously. The non-monotonous variation of $\mu_{\perp}$ during compression may be due to the fact that molecular dipole moments are not parallel to the molecular chains. The vertical orientation of the molecular dipole moment and the vertical molecular orientation may not be coinciding, and $\mu_{\perp}$ is supposed to reach its maximum value at larger areas per molecule. Thus it is not the necessary condition for the head group conformation to change with compression [41]. A π - π stacking attractive force is formed between molecules. The π electron cloud of one benzene ring attracts towards that of another, shifting its electrons away from the other benzene molecule as negative charges repel each other. This creates a new positive dipole, which subsequently attracts the electrons cloud from the π bond of second benzene, which shifts towards positive dipole.

3.3. Fourier transform infrared spectroscopy:

Fourier transfer infrared (FTIR) spectroscopy profile of PANi is shown in Figure 3.7 The main characteristic bands of PANi are assigned as follows: the peak at 3456.12 cm^{-1} is attributed to N-H stretching mode, the peaks at 1565 cm^{-1} and

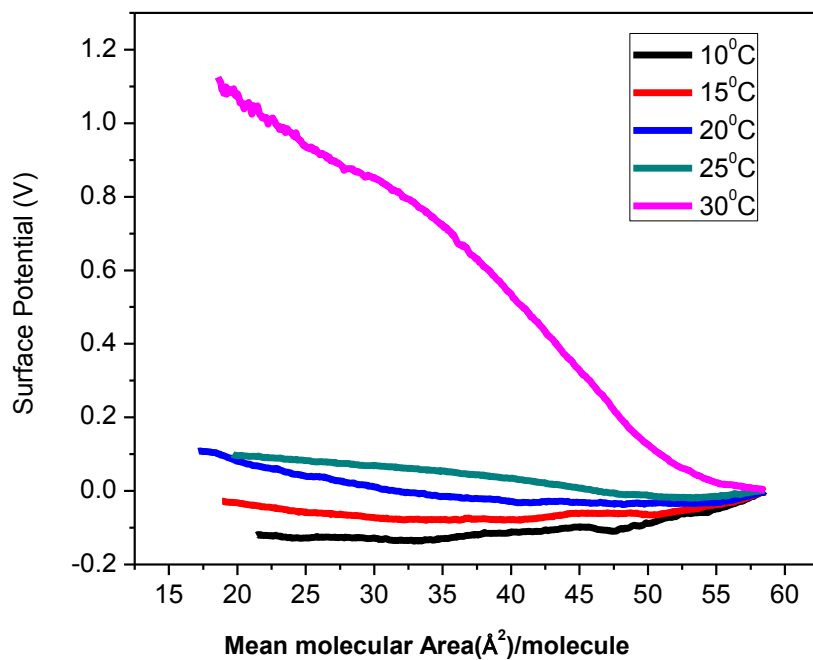


Figure 3.5: Surface Potential-Area (ΔV -A) isotherm at various temperatures for PANi monolayer.

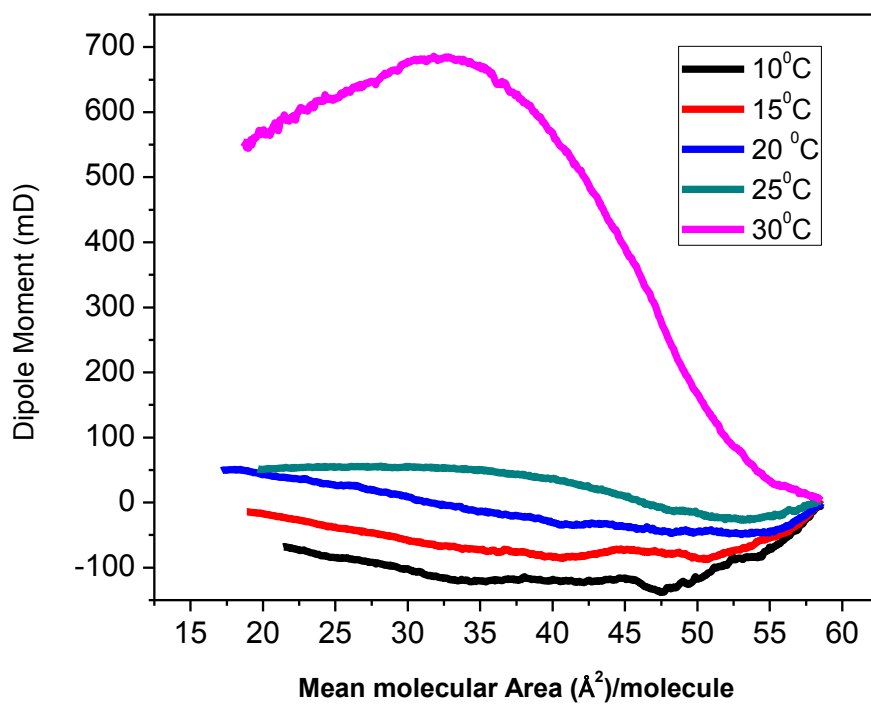


Figure 3.6: Dipole moment-Area ($\mu_{\perp}$ -A) isotherm at various temperatures for PANi monolayer.

1487 cm^{-1} are associated with C=N and C=C stretching mode for the quinonoid and benzenoid rings, The peaks at about 1299 cm^{-1} is due to C-N stretching mode of benzenoid ring, whereas the peak at 1145 cm^{-1} is assigned to quinonoid unit of doped PANi and the peak at 876 cm^{-1} was assigned to out-of-plane bending vibration of C-H of 1,4 substituted benzenoid rings, which confirmed the formation of PANi [45,46]. The results show that obtained PANi contains 1, 4-para-disubstituted linear chains. The FTIR spectrum of 22 monolayers at the air–solid interface is shown by dotted line in Figure 3.7. 22 monolayers of PANi when transferred to substrate, at transfer ratio (t_r) nearly 1, it confirms presence of all functional groups. So, transfer of PANi was done successfully.

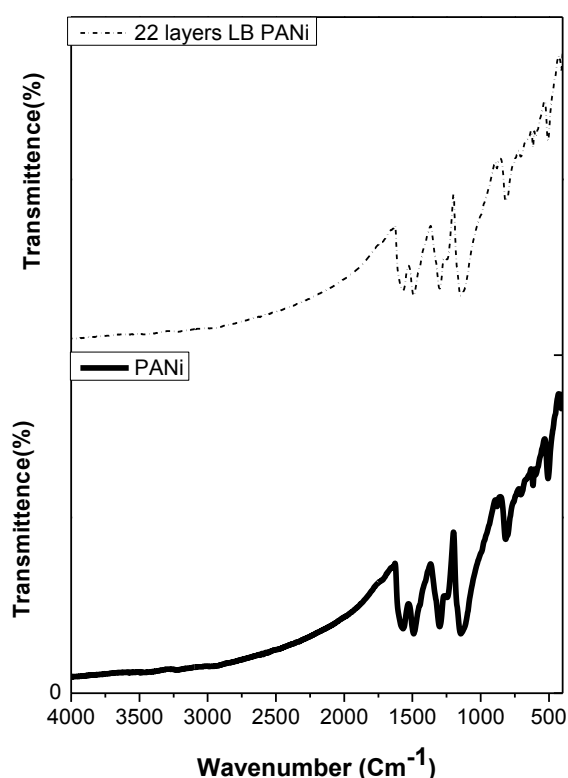


Figure 3.7: Fourier Transform Infrared spectroscopy profile of PANi powder and PANi LB film (22 multilayers).

3.4 Electron Absorption Spectroscopy

Figure 3.8 shows spectra of pure PANi, in NMP between 300 nm and 1000 nm. The spectra of PANi show two characteristic bands at 320 nm and 630 nm, respectively. The 320 nm band is attributed to a p-p* transition in the benzenoid ring. The absorption in the visible range, at 630 nm, is attributed to the p–polaron transition in the quinoid rings. The

spectra are characteristic for the emeraldine base formed upon the deprotonation action of NMP on the PANi salt. Excess of NMP leads to deprotonation of salt to emeraldine base. This is due to the C=O groups in NMP that forms hydrogen bonds with the dopant acid and inhibits the doping process [47, 48].

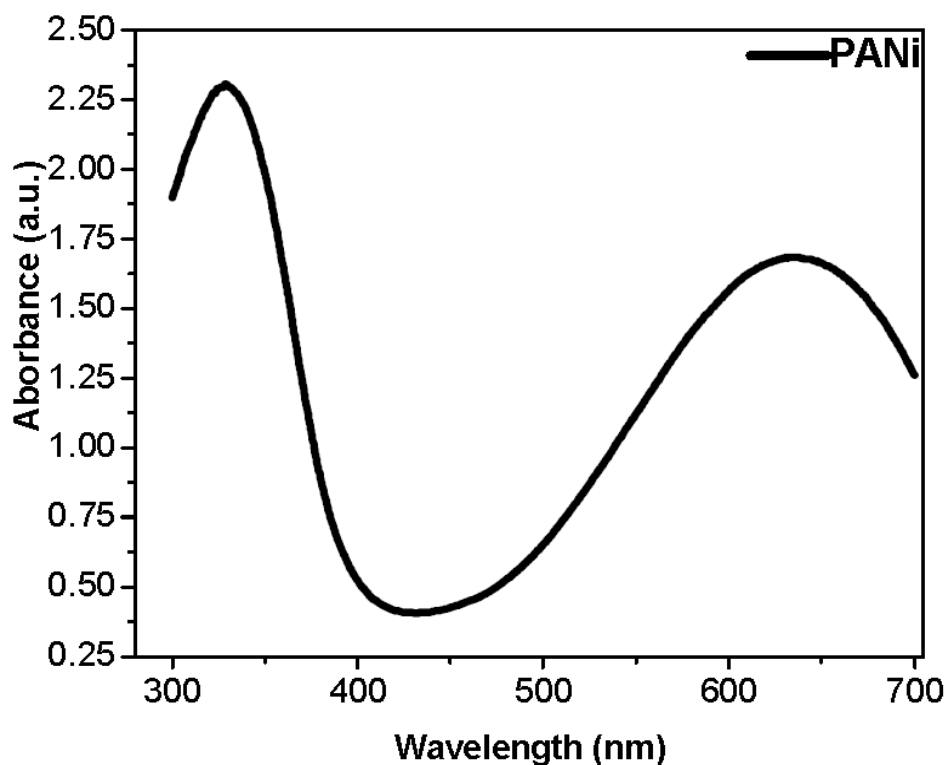


Figure 3.8: UV-Visible spectra of PANi in NMP.

3.5 X-ray diffraction of PANi LB film

Figure 6(i) shows the X-ray diffraction profile of 22 multilayers, LB films of PANi deposited on quartz substrate, when exposed to Cu- α radiation source from X-ray diffractometer. Most forms of PANi are amorphous showing the presence of broad high-angle asymmetric scattering peak stretching from 2θ between 15° and 25° . The peaks of the synthesized PANi show broad peaks (of less intensity) situated at $2\theta = 21.23^\circ$ and 25.72° corresponding to d-spacing of $4.18 \text{ \AA}$ and $3.54 \text{ \AA}$ and with planes of (010) and (200). It indicates the presence of benzene rings and polymeric nitrogen. This d-space is the distance between the adjacent benzene rings planes and is the interchain or close contact distance between two adjacent chains [49, 50].

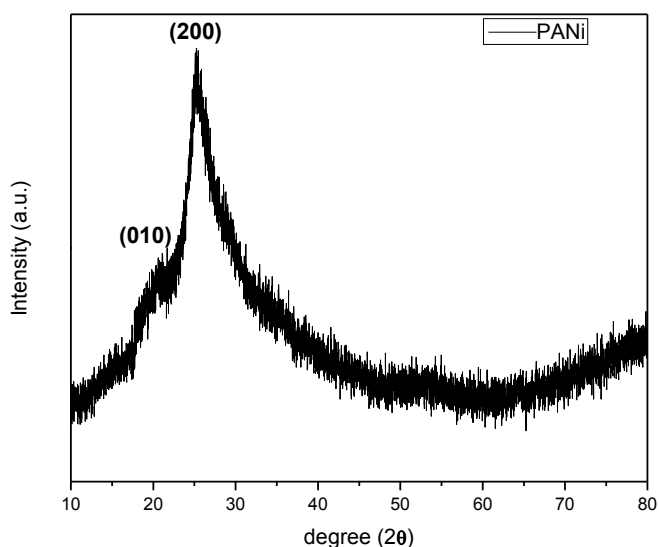


Figure 3.9: X-ray diffraction pattern of PANi LB film.

3.6 Atomic Force Microscopy of PANi LB Films

The PANi LB film was scanned under atomic force microscope (AFM) (Solver-NEXT NT-MDT) equipped with Silicon nitride (SiN) probe in noncontact mode. It has tip curvature radius 6 nm, attached to a cantilever having resonance frequency (87–230 kHz), and force constant 5.1 N/m.

3.6.1 Topography of ITO coated glass substrate and PANi LB film

Figure 3.10 show average height profile of non-contact atomic force microscopic (AFM) mode image, scan range $2 \times 2 \mu\text{m}^2$, scan rate 1 Hz of (a) ITO coated glass substrate 2D image, (b) PANi LB monolayer (c), (d) their three dimensional (3D) topography views. The average height of ITO coated glass substrate is 1.4 nm which ensures its suitability for deposition of Langmuir monolayer [51]. The AFM image of the PANi film surface shows polycrystalline morphology formed from nanometer-length fibrils with strong π - π stacking arrangement parallel to the surface of film.

3.6.2 Phase Imaging

Phase Imaging or phase detection microscopy (PDM) is obtained when AFM is operating in Non-Contact AFM mode. It is the monitoring of the phase lag between the signal driving the cantilever oscillation and the output signal of cantilever oscillation, as shown

in Figure 3.11. Variations in the phase lag reveal changes in the surface properties such as friction, adhesion and elasticity. The phase images are recorded simultaneously with the topographical images in Non-Contact AFM mode.

Phase imaging is suitable technique to collect information of properties of materials like LB films, polymers whose topography is not clearly visible by contact mode AFM; thus providing complementary information to the topography image.

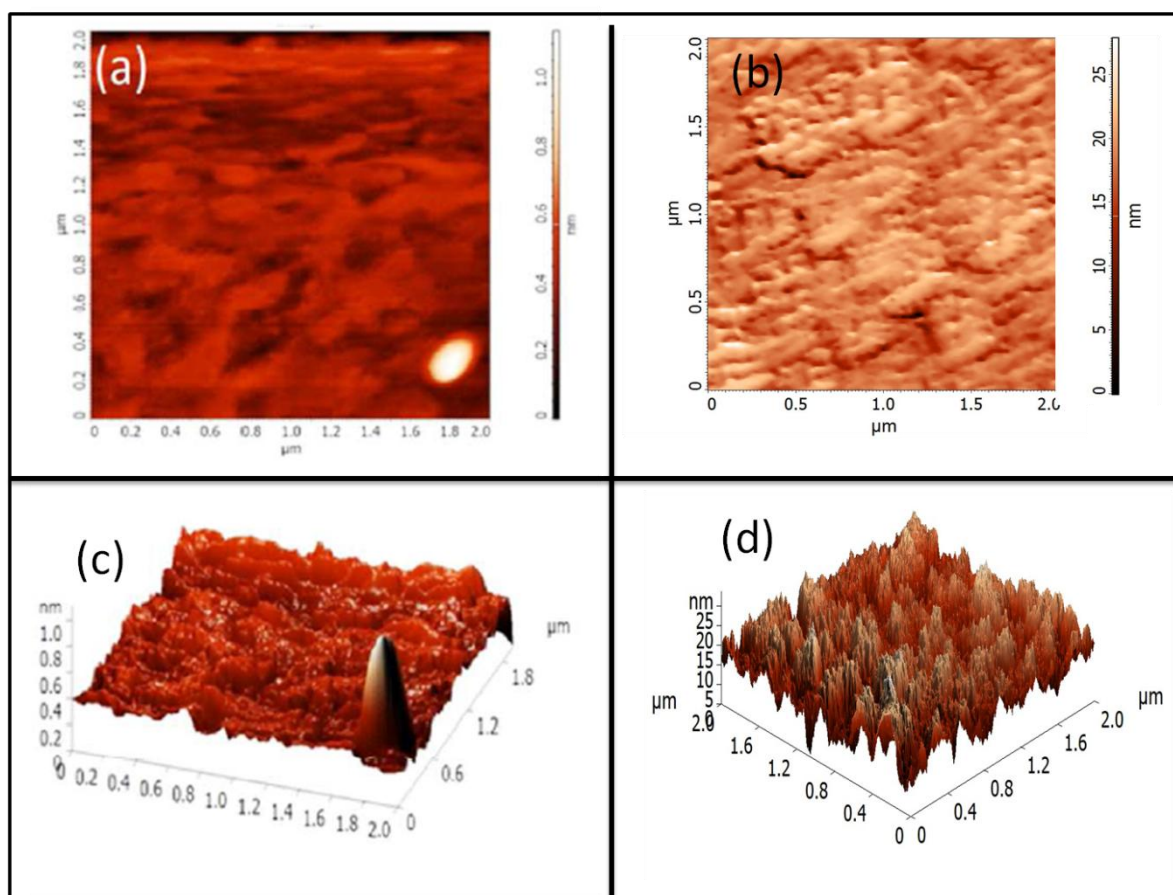


Figure 3.10: Non-contact mode atomic force microscopic (AFM) image, scan range $2 \times 2 \mu\text{m}^2$, scan rate 1 Hz (a) height profile of ITO coated glass substrate 2D image, (b) height profile of PANi LB monolayer (c), (d) their 3D views.

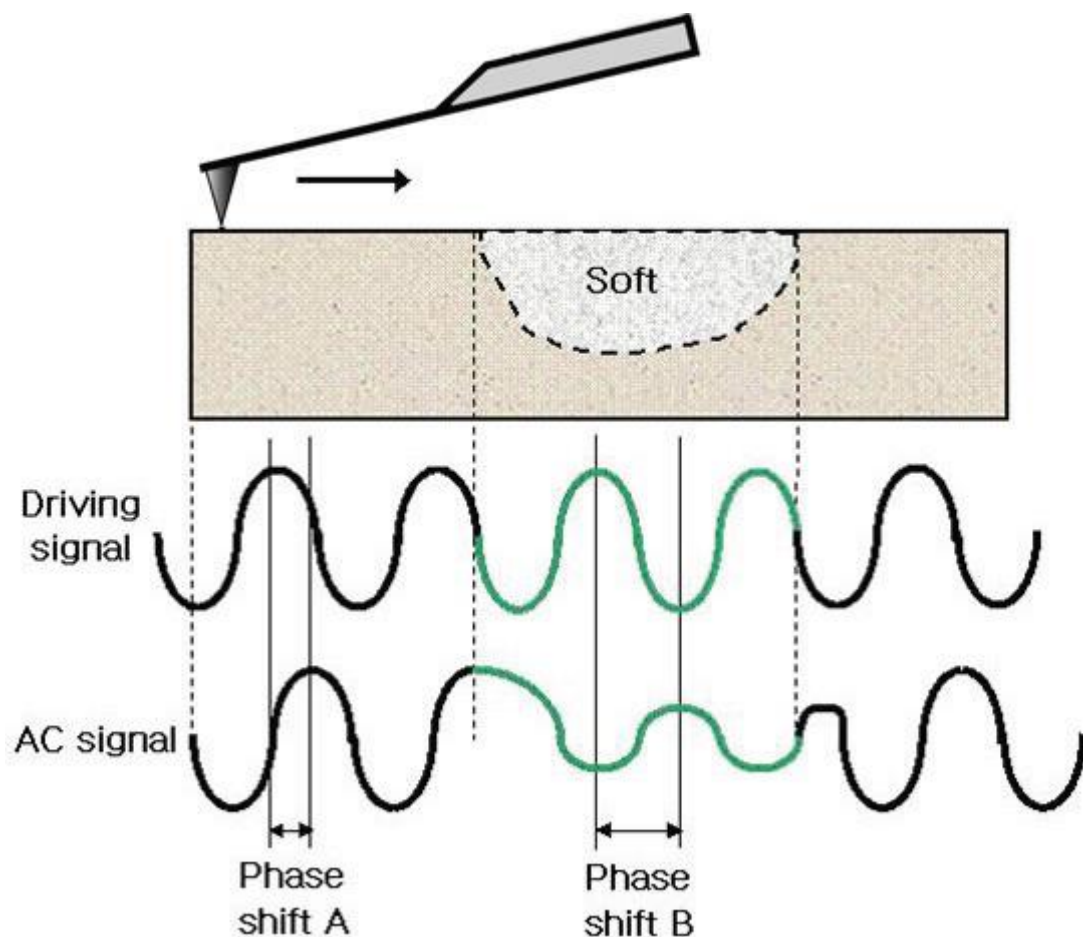


Figure 3.11: Schematic of phase detection microscopy of the sample surface [52].

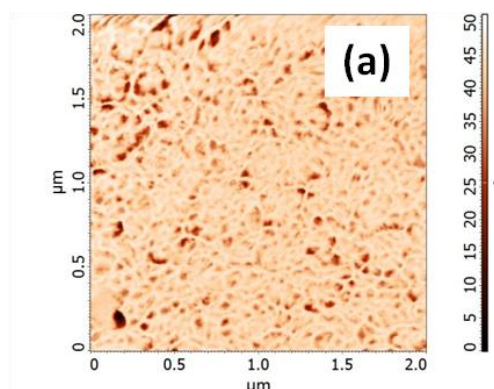


Figure 3.12: Atomic force microscopy (AFM) Phase image of polyaniline Langmuir-Blodgett (LB) film.

Phase detection microscopy detects variations in composition. Cylindrical, interconnected nanofibrillar network kind morphology is observed in phase image of the deposited LB films of PANi as shown in figure 3.12.

3.6.3 Conductive Atomic Force Microscopy

Contact mode topography and conductivity measurements of the PANi LB films were performed using a conductive (Pt-coated) cantilever (NT-MDT, CGS-01/Pt; frequency 4-17 kHz; force constant 0.03 N/m, curvature radius of the tip is 35 nm). PTB certified Test grating TGQ1-41680-09 (company NT-MDT) is used to calibrate the AFM in X, Y and Z directions. Basic step height can vary from the specified one within $\pm 10\%$. The ITO coated glass was mounted on a special substrate (supplied with the Solver-NEXT) having a spring contact for conductivity analysis. The contacts on the film were provided by silver nano paint (SPI Ag Colloid). The topographic data was scanned in a grid of 512×512 pixels and scan size was $2 \times 2 \mu\text{m}^2$.

Figure 3.13(a) shows $2 \times 2 \mu\text{m}^2$ surface topography image of ITO substrate taken in contact mode. Its corresponding 3D image is shown in Figure 3.13(b). The average height of ITO substrate measured by the software NOVA P9 NTMDT (Image Analysis 2.1.0.800) is 1.4 nm and root mean square (rms) roughness is 1.04 nm and surface roughness average is 1.03 nm; this proves the smoothness of substrate and its suitability for deposition of Langmuir monolayer.

Figure 3.13 (c) shows $2 \times 2 \mu\text{m}^2$ surface topography image of PANi LB film on the ITO substrate taken in contact mode. Its corresponding 3D image is shown in Figure 3.13(d). PANi LB film has homogeneous topography with average height profile of range 25 nm, root mean square roughness of 2.1 nm and surface roughness average of 1.6 nm [53].

Surface conductivity mapping has been obtained by operating the Scanning Probe Microscope (SPM) in conductive AFM (C-AFM) mode. In C-AFM, during imaging, the conductive cantilever scans the surface of PANi LB film in contact mode to produce a topographic image and also map the electric current between the cantilever and the sample simultaneously. The scheme of electronic circuit used to measure the current flowing through the LB film is shown in Figure 3.14. The average current of C-AFM image was determined by software (NOVA P9 NTMDT (Image Analysis 2.1.0.800)). A metallized AFM tip is used as a mobile electrode [54].

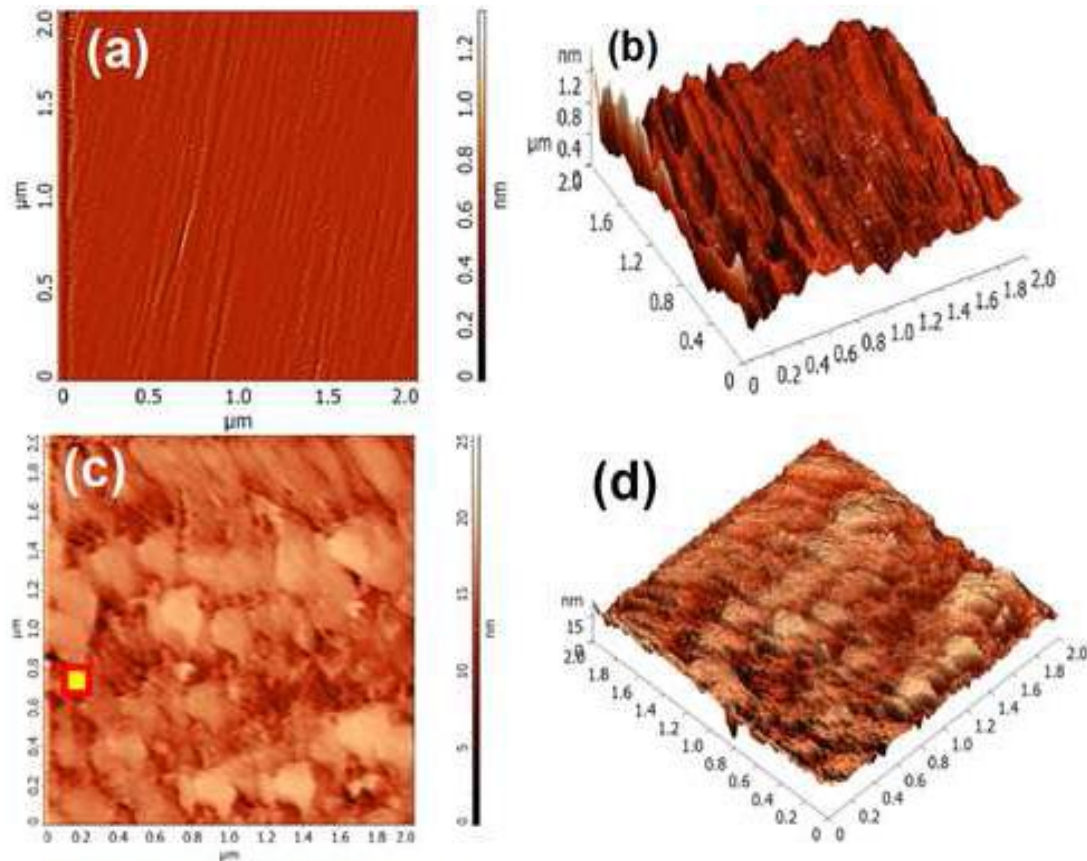


Figure 3.13: Contact mode atomic force microscopic (AFM) image, scan range $2 \times 2 \mu\text{m}^2$, scan rate 1 Hz (a) height profile of ITO coated glass substrate 2D image, (b) its 3D view, (c) height profile of PANi LB monolayer, (d) its 3D view.

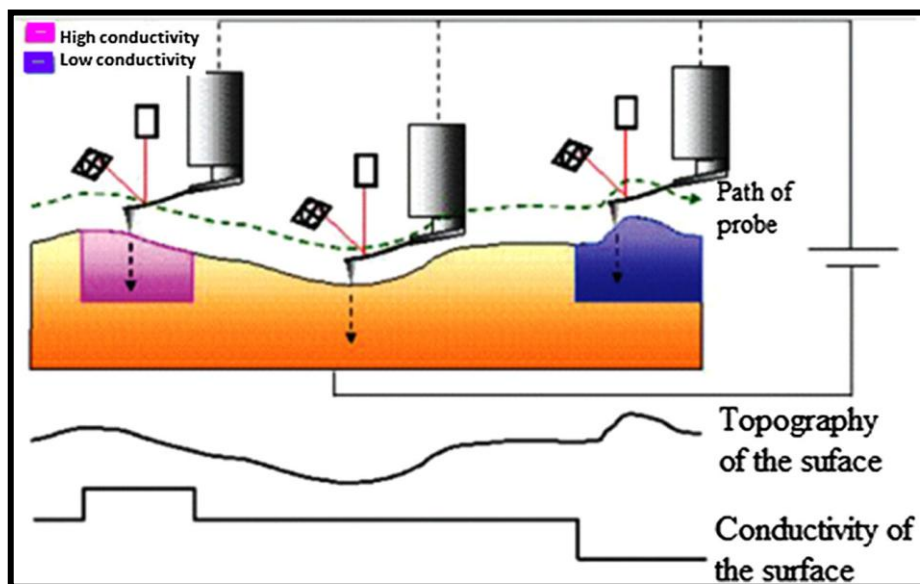


Figure 3.14: Schematic diagram of the conductive AFM system.

At a given voltage, the current measured by the instrument is given by the total circuit resistance, which is the sum of the resistance of the sample, tip and contact resistance between the sample and the tip; the latter two resistances can be assumed constant and negligible compared to the sample. Once the scanning is complete, local I-V characteristic curves can be obtained by measuring the current at a selected point of the scanned area; as a function of bias voltage applied in a defined range (up to a maximum of -10V to +10V). The AFM cantilever tip has contact size of few nanometer squares, so, the variation of the local electrical properties in the nanoscopic level, can be obtained by I-V curves. Fig. 3.15 show single-point current vs. voltage (I-V) curves for PANi LB film on the ITO substrate corresponding to the point marked on image 3.13 (c). The data presented is the result of single I-V measurements by software NOVA P9 NTMDT 2.1.0.800 and no averaging of curves has been performed. The I-V measurements demonstrate semiconducting behaviour of PANi and PANi-ZnO nano-composite LB films. The I-V characteristics show currents ranging up to 5 nA in PANi LB film [55].

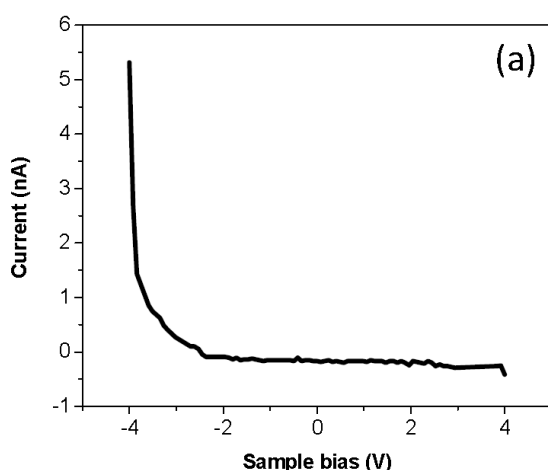


Figure 3.15: The I-V characteristics show currents ranging up to 5 nA in PANi.

Fig. 3.16 (a) show conductive data images of PANi LB film on the ITO glass substrate obtained with an applied bias voltage of 4V and are recorded simultaneously with topographical images 3.13(c) [56]. Current distribution up to 5 nA in PANi LB film is shown in Fig. 3.16(a) and in its corresponding 3D image (Fig. 3.16(b)). The distribution of current on the whole surface of PANi LB film is almost uniform and almost homogeneous charge transport current have been observed in the surface conductance of the PANi LB film. This shows the film is electrically homogeneous. The current homogeneity is also indicating to the homogeneous doping of the PANi.

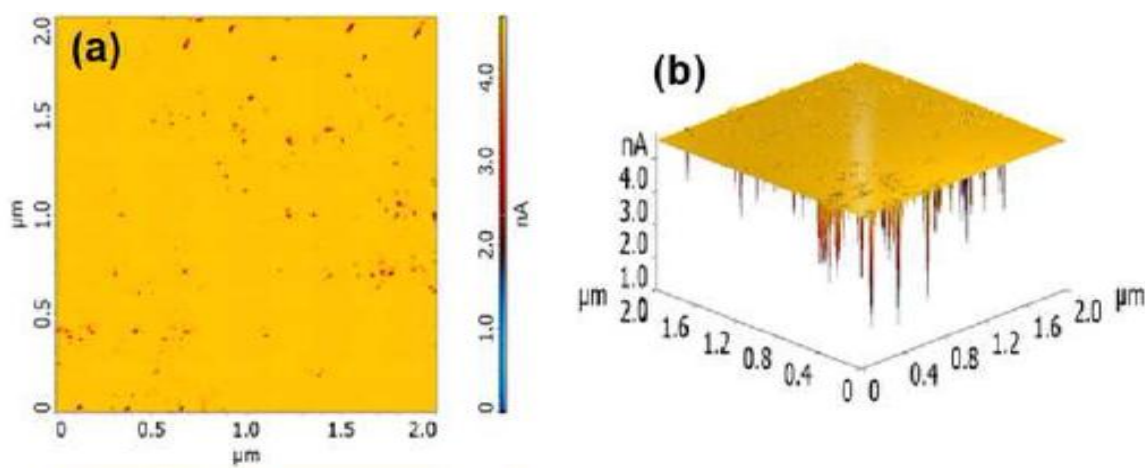


Figure 3.16: Conductive data images, obtained with an applied bias voltage of 4 V, of: (a) PANi and (b) its corresponding 3D image on the ITO substrate.

3.7 Conclusions

It is concluded that the semi-amphiphilic nature of the PANi played a vital role in the orientation and ordering of films at interface. Reproducibility of the π -A isotherm confirmed the stability of the mono-layer. Electrical effects in Langmuir monolayers are investigated by surface potential and dipole moment of PANi at various temperatures is calculated using Helmholtz equation and these increases with temperature and becomes +ve at room temperature. Investigations of surface potential of fluid interfaces can be a valuable tool for description, interpretation and evaluation of physical properties of monolayers as well as characterization of structure. Fourier transform infrared spectroscopy, UV-visible spectroscopy and X-ray Diffraction study indicates formation of PANi LB Films. The topography of Langmuir-Blodgett films characterized by atomic force microscopy show average height profile of 25 nm. The phase imaging show composition of PANi throughout the film surface and interconnected nanofibrillar network kind morphology. Local Current-voltage (I-V) spectroscopy results by C-AFM show semiconducting behaviour of PANi LB film. Conductive data image show almost uniform current distribution through the PANi LB films. Thus LB technique provides new insight into the ultrathin films of conducting polymers, which will find a variety of applications in sensor devices. This suggests the possibility of using PANi ultrathin films

in many important applications in conducting polymer based electronics and sensor devices.

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CHAPTER - 4

Hybrid Polyaniline–TiO₂ Nano-composite Langmuir–Blodgett Thin Films: Self-Assembly and Their Characterization

Overview

Polyaniline (PANi)–titanium dioxide (TiO₂) nano-composite (5, 10, 15, 20 wt %) materials are prepared by chemical polymerization of aniline doped with TiO₂ nanoparticles. Surface pressure–area (π -A) isotherms of these nano-composites show phase transformations in the monolayer during compression process at various temperatures. Multiple isotherms indicate that the monolayer of the nano-composite material can retain its configuration during compression-expansion cycles. Fourier transfer infrared spectroscopy and UV–visible spectroscopy study indicates the presence of TiO₂ in PANi, whereas X-ray Diffraction study confirmed the anatase phase of TiO₂ and particle size ($\sim$ nm) of PANi–TiO₂. The morphology of Langmuir–Blodgett films of these nano-composites was also characterized by atomic force microscopy in non-contact mode as well as in contact mode. Phase imaging revealed the inclusion of TiO₂ in the polymer matrix, which occurs during the film formation. The electrical properties of PANi–TiO₂ nano-composite LB films investigated by CAFM show local I-V characteristics and conductive data images.

4.1 Introduction

In previous chapter 3 the Langmuir-Blodgett films of PANi have been studied. Now we are going to study effect of nanoparticles doping on behavior of PANi. The electronic properties of the conducting polymers can further be enhanced by tailoring them with metal oxides. Titanium dioxide (TiO_2) being nontoxic, insoluble, inexpensive, and chemically stable, emerged as one of the most suitable doping agents in PANi. Due to their electrical and optical properties, TiO_2 nanoparticles find applications in a variety of sensors [1-3] and reflectors [4-7]

The preparation of PANi- TiO_2 nano-composites is standardized because of their well-matched band gap for the charge transfer. TiO_2 anatase is a typical n-type wide gap semiconductor (~ 3.2 eV), whereas PANi is considered to be a p-type material having a wide band gap (~ 3.6 eV). It has been observed that the n-p contacts between TiO_2 and PANi matrix increases the physical adsorption sites for gas molecules thus improving the gas sensing features of PANi- TiO_2 nano-composites [8-10]. Some recent reports show that these materials have also been applied in newer applications like electrically conductive textiles, sensors, and photosensing applications with their reasonable photocatalytic and enhanced optical activity etc. [11-17].

The metal-organic semiconductor materials are expected to be substitutes of the metal-inorganic semiconductor materials to provide economical flexible electronic devices [18–20].

Thus, several research groups investigated physical aspects of polymeric thin films deposited by Langmuir-Blodgett technique [21–24], but the behavior of Langmuir monolayer and LB films of PANi- TiO_2 nano-composite systems is still at infancy. In this chapter, I report the synthesis and characterization of hybrid PANi- TiO_2 nano-composite materials by chemical route and depositing their ultrathin films by LB method. In this chapter, an attempt is made to understand the effects of TiO_2 nano-particle doping on properties of PANi- TiO_2 thin films at air–water and air–solid interfaces. Monolayers at air–water interface were characterized by surface pressure–area (Π –A) isotherms. X-Ray diffraction is used to study the phase transition of LB films deposited on glass substrates, Fourier Transform Infrared Spectroscopy to study interaction between nanoparticles and polymer matrix and atomic force microscopy (AFM) is used to investigate topography of deposited LB films.

The reaction mechanism for PANi–TiO₂ nano-composite showing polymerization of aniline on the surface of TiO₂ nanoparticles is shown in Figure 4.1(a). The average molecular length of monomer was ~5 Å (as determined from its molecular structure by software) Figure 4.1 (b) shows the molecular model representing the position of TiO₂ in the PANi chain molecules as sketched using ACD/Chem. Sketch software (Advanced Chemistry Development, Inc, version 11.01) [25].

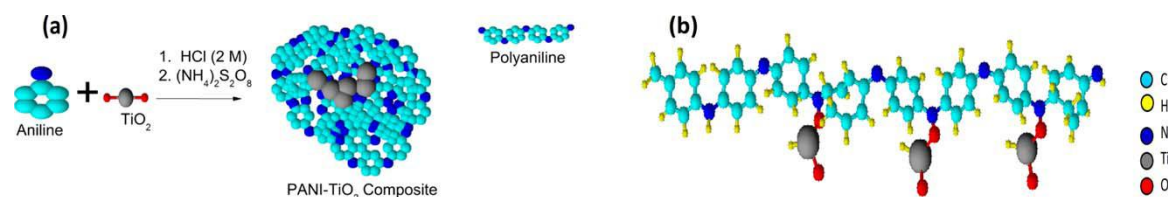


Figure 4.1: (a) Schematic of the reaction mechanism for PANi–TiO₂ nano-composite showing polymerization occur over the surface of TiO₂ nanoparticles, and (b) molecular model representing the position of TiO₂ in the PANi chain molecules as sketched using ACD Chem software.

4.2 Fourier Transform Infrared (FTIR) Spectroscopy of PANi–TiO₂ nano-composites

Fourier transfer infrared (FTIR) spectroscopy profile of PANi, TiO₂, and PANi–TiO₂ nano-composites (5, 10, 15, 20 wt %) is shown in Figure 4.2. The main characteristic bands of PANi are discussed in previous chapter 3. Figure 4.2(b) shows a broad peak between 800 and 465 cm⁻¹ assigned to the Ti-O-Ti stretching vibrations with a valley centered at 503 cm⁻¹. The band Ti-OH observed below 3500 cm⁻¹ indicates the existence of hydrogen bonding [26, 27]. For the PANi–TiO₂ nano-composites (20 wt %), the characteristic peaks of PANi around 1299 cm⁻¹, 1495 cm⁻¹, and 1581 cm⁻¹ shifted to higher wavenumbers of 1301 cm⁻¹, 1492 cm⁻¹, and 1575 cm⁻¹ after TiO₂ was introduced indicating a slight effect of TiO₂ on the bonds involved in these bands. Figure 4.2(f). The characteristic peak of the N-H stretching mode at 3456 cm⁻¹ of PANi shifted to a lower wavenumber (3417 cm⁻¹) in the PANi–TiO₂ nano-composite, and the hydrogen bond absorption at 3210 cm⁻¹ was strengthened after TiO₂ was introduced. Titanium is a transition metal element, so TiO₂ has a strong tendency to form coordinate bond with the nitrogen atoms in PANi [28]. From the spectrum of PANi–TiO₂ nano-composite, it was realized that a strong interaction exists between PANi and TiO₂ particles, and the

polymerization of aniline occurs on the surface of TiO_2 nanoparticles. Similar shifts of peak positions in PANi- TiO_2 (5, 10, 15 wt %) nano-composites have been observed as shown in Figure 4.2(c-e) [25, 29].

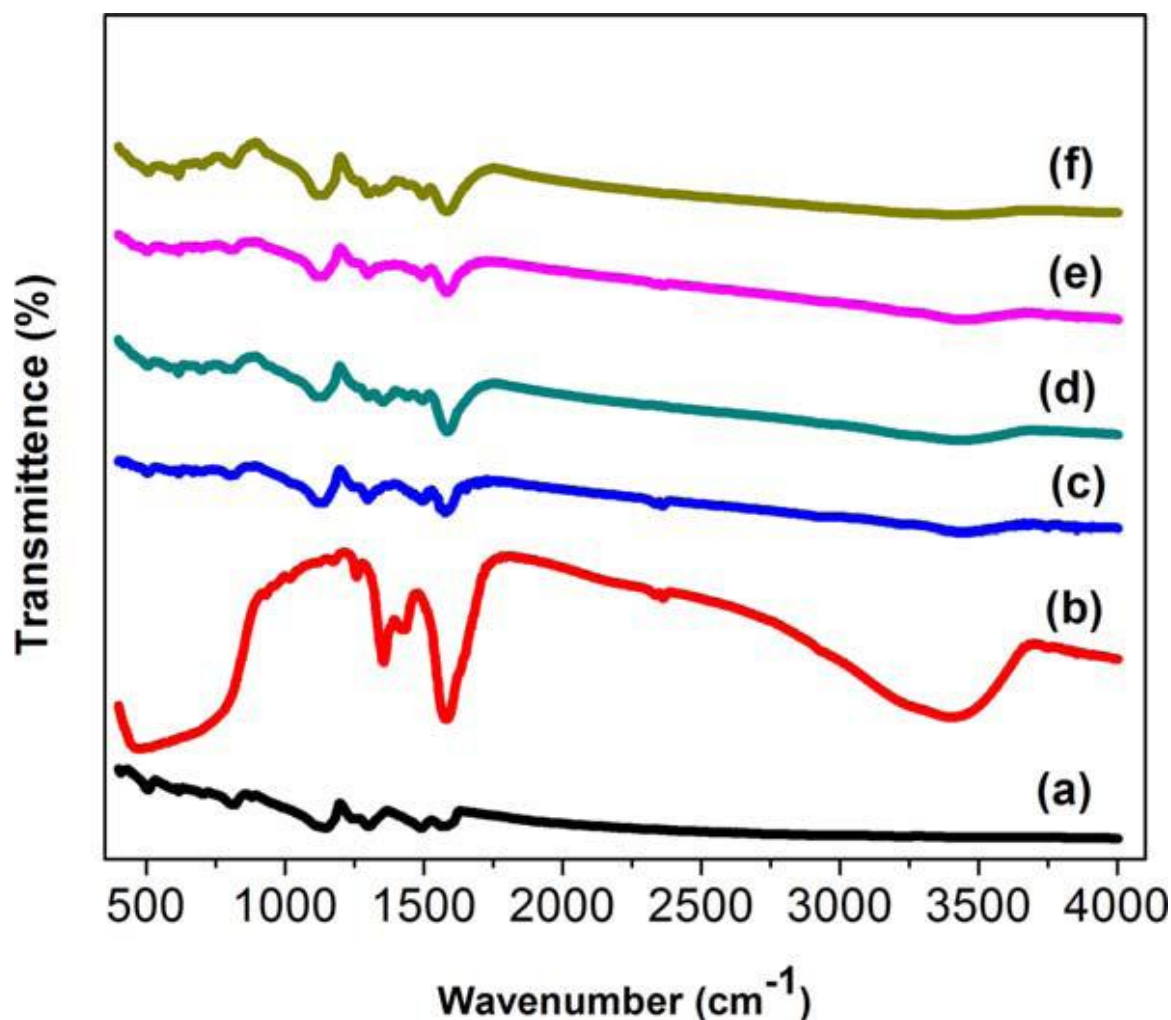


Figure 4.2: FTIR profile of the (a) PANi, (b) TiO_2 nanoparticles, (c) 5, (d) 10, (e) 15, (f) 20 wt % TiO_2 in PANi- TiO_2 nano-composite.

4.3 Monolayer at Air–Water Interface:

4.3.1 Surface Pressure- Area (π -A) Isotherms of PANi- TiO_2 (5, 10, 15, 20 wt %) nano-composite systems

The spreading solutions of PANi- TiO_2 (5, 10, 15, 20 wt %) were prepared in NMP and particle concentration was 0.2 mg/mL. The proper dissolution of nano-composite in NMP

was ensured by uniform solution obtained after sonication. 200 μL of all the solutions was spread on the ultrapure Milli-Q3 (pH=6.00) water subphase contained in trough by using Hamilton micro syringe separately [30, 31] The solvent settled down in about 30 min before the area enclosed by the barriers (delrin) was reduced at 10 mm min^{-1} to compress the molecules on the water surface.

The surface pressure- mean molecular area (π -A) isotherms of PANi-TiO₂ (5, 10, 15, 20 wt %) nano-composite materials are shown in Figure 4.3. The isotherms indicate the formation of stable monolayers at constant compression speed of 10 mm min^{-1} . A_i represents lift off area; at this point, compression of monolayer just starts and, with constant compression by using barriers, we reached at condensed phase (A_0). In region (I), minimum change is seen in the surface pressure; monolayer is in the gaseous phase starting from lift off area (A_i) $\sim 70.09\text{ \AA}^2/\text{molecule}$. Surface pressure varies from 0.06 to 0.80 mN m^{-1} . On further compression, monolayer attained expanded liquid phase from gaseous phase as indicated by region (II). In PANi isotherm, increase in compression resulted in orientation and ordering of molecules at air-water interface. Initially molecules were in gaseous phase but then alignment of monolayer increased surface pressure up to 30 mN m^{-1} (chapter 3). Surface pressure variation of 5 wt % PANi-TiO₂ nano-composite indicates that molecules are getting aligned with an increase in mean molecular area per molecule. In this case, in region (III) surface pressure of well aligned monolayer rise up to 7.5 mN m^{-1} this is lower than surface pressure attained by pure PANi, hinting at the influence of 5 wt% TiO₂ present at the interface. At this pressure a condensed phase is formed.

Surface-pressure variation of 10 wt% TiO₂ in nano-composite at constant barriers compression 10 mm min^{-1} indicates that the molecular alignment as a function of expanded surface area. The size of nanoparticles is about 25 nm which is much more than that of the monomeric units of PANi which has average length of $5\text{ \AA}$ [25, 32]. In this case, surface pressure of well-aligned monolayer rises up to 13 mN m^{-1} , Whereas isotherm for 15 and 20 wt% TiO₂ nanoparticles in PANi reveals smooth transitions from the gas to the liquid phase and from the liquid phase to the condensed phase at 14.5 mN m^{-1} and 15 mN m^{-1} respectively. At this surface pressure, the molecules are relatively close packed and have very little room to move. This may be due to the reason that the high surface energy of the nanoparticles might be responsible for the decrease of free volume for the orientation of polymer chains. Hence, the doping of TiO₂ in PANi

increases condensed area (A_0) as seen in Figure 4.3. It indicates that TiO_2 nanoparticles are influencing the orientation of monolayer of polymer matrix.

The surface pressure-area isotherms of the monolayer show a considerable shift in the isotherms towards higher area per molecule on increasing the concentration of TiO_2 . The surface pressure-area isotherm of nano-composite materials indicates good surface spreading properties of monolayer.

Figure 4.4 show π -A isotherm profile of PANi- TiO_2 (20 wt %) nano-composite monolayer at various temperatures. Isotherm behavior is not much affected with the variation of temperature. There is a slight increase in surface pressure with rise in temperature which may be due to the change in surface tension of subphase water with variation of temperature but the film remains stable.

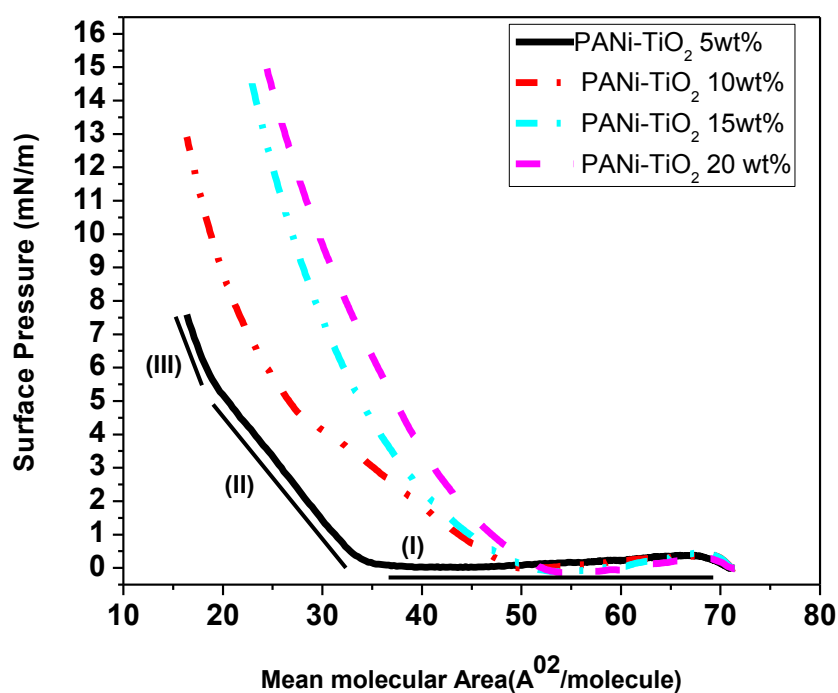


Figure 4.3: Isotherms of (5, 10, 15, 20) wt % TiO_2 in PANi- TiO_2 nano-composites.

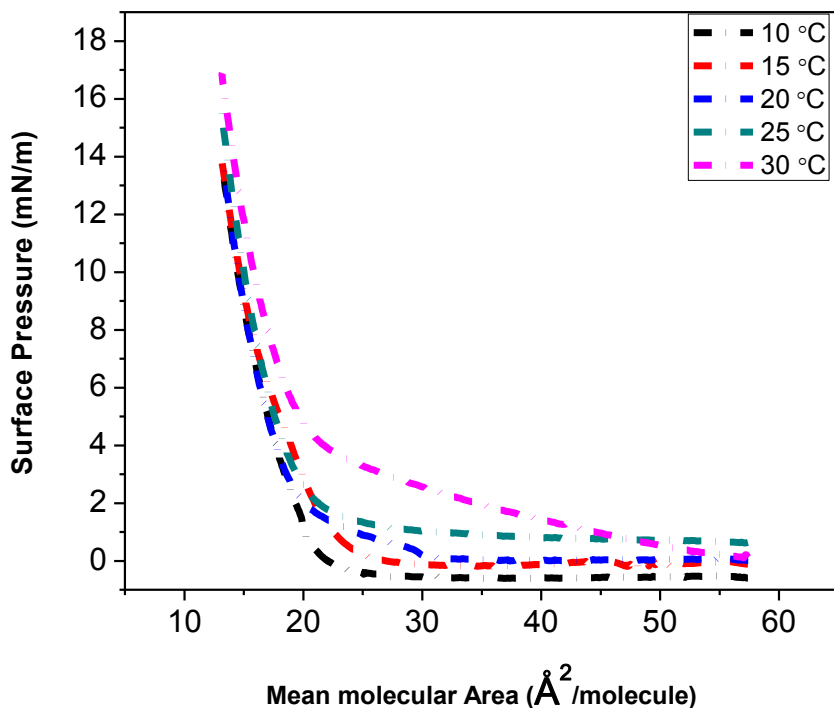


Figure 4.4: π -A isotherm profile of PANi-TiO₂ monolayer at various temperatures.

4.3.2 Hysteresis in π -A Isotherms

The stability of the film over water surface for PANi-TiO₂ nano-composite was studied by running three complete cycles in range of (0–10) mN m⁻¹ as shown in Figure 4.5.

Compression isotherms show monolayer compressed to a predetermined pressure and then decompressed. It is found that continuous compression–expansion cycles have negligible hysteresis with almost zero shifting in each cycle. The compression–expansion curves in second and third cycle almost resembled the compression curve, indicating negligible hysteresis. It establishes the stability of the monolayer at water surface. These stable films were easily transferred to substrates by using Y-type deposition method [33, 34].

Monolayers and 25 multilayers of nano-composites were successfully transferred to Indium tin oxide (ITO) coated conducting glass and quartz substrates.

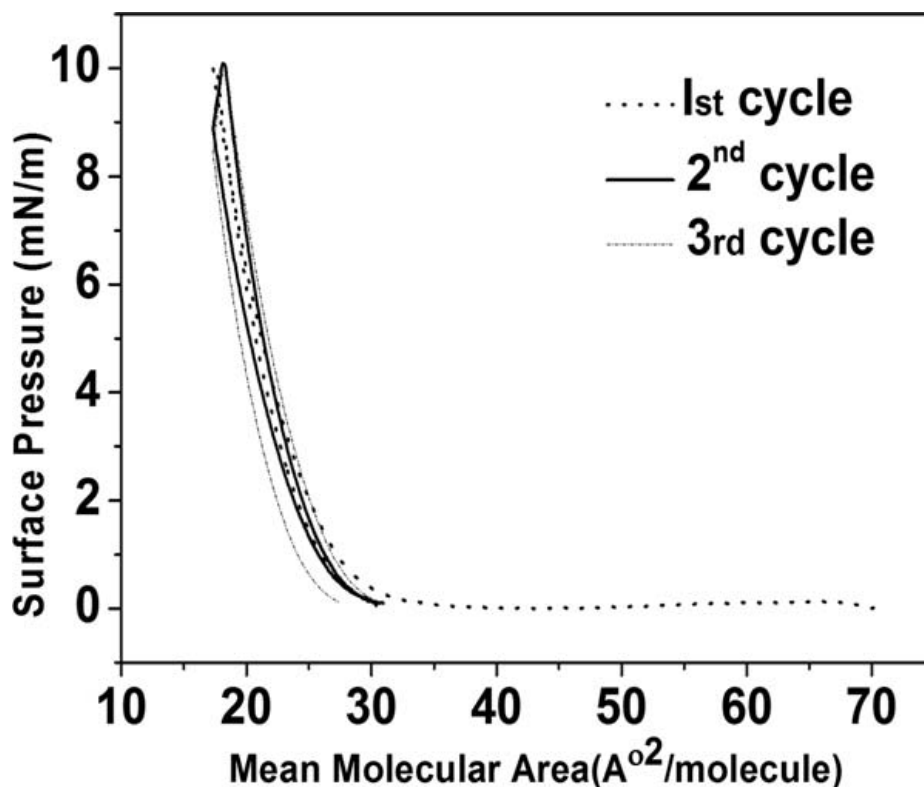


Figure 4.5: Π -A multiple isotherms profile of PANi-TiO₂ (20 wt %) nanocomposite monolayer, particle concentration 0.2 mg/mL in NMP solution, spreading amount 200 μ L, target pressure 10 mN/m, rate 10 mm²/min.

4.4 Electron Absorption Spectroscopy

Figure 4.6(i) shows spectra of pure PANi, PANi-TiO₂ (5, 10, 15, 20 wt %) nanocomposites, and TiO₂ nanoparticles in NMP between 300 nm and 1000 nm recorded by using UV-visible spectrophotometer (Analytic Jena, SPECTROD 205). PANi as well as PANi-TiO₂ nano-composites are soluble properly in NMP. Figure 4.6(i) indicates that pure TiO₂ absorbs light of wavelengths below 400 nm (UV region) only, whereas PANi-TiO₂ nano-composites have broad absorbance in the UV and visible regions. The position of the 630 nm absorption band in case of PANi is little shifted in PANi-TiO₂ nano-composites with variation in concentration of TiO₂. In PANi-TiO₂ (20 wt %) nano-composites, the peak at 320 nm and 630 nm in PANi shifts to 340 nm and 648 nm. The broad absorption band around 648 nm follows a long tail in the visible-light region. The

tail is indicative of charge carrier delocalization in the polaron band favored by an extended chain conformation. Therefore, PANi–TiO₂ nano-composites can be excited to produce more electron–hole pairs under visible-light illumination and this is expected to increase photocatalytic activities [35]. As there is little red shift in case of PANi–TiO₂ (20 wt %) nano-composites, so we choose it for further investigations. The UV–Vis spectra of LB film of 25 layers of PANi–TiO₂ (20 wt %) nano-composites on quartz substrate is shown in Figure 4.6(ii).

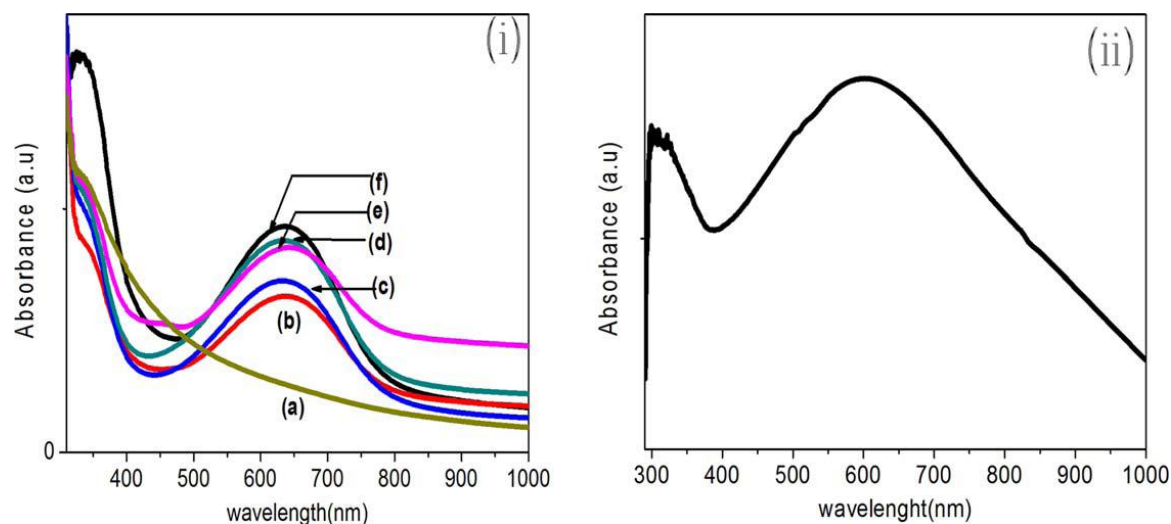


Figure 4.6: (i) UV–visible spectra of the (a) TiO₂ nanoparticles, (b) 5, (c) 10, (d) 15, (e) 20 wt % TiO₂ in PANi–TiO₂ nano-composite and (f) pure PANi; (ii) UV–visible spectrum of LB film of 25 layers of PANi–TiO₂ nano-composite.

The two electronic transitions at 320 nm and 604 nm are observed. These peaks arise due to the transition from a polaron to bipolaron lattice [36]. The position of the 630 nm absorption band is little shifted with film thickness. Similar peaks were observed in single monolayer but with very low intensity. The absorbance peak increases with the number of deposited layers indicating that a suitable multilayer build-up is achieved.

4.5 X-Ray Diffraction Spectroscopy of LB films

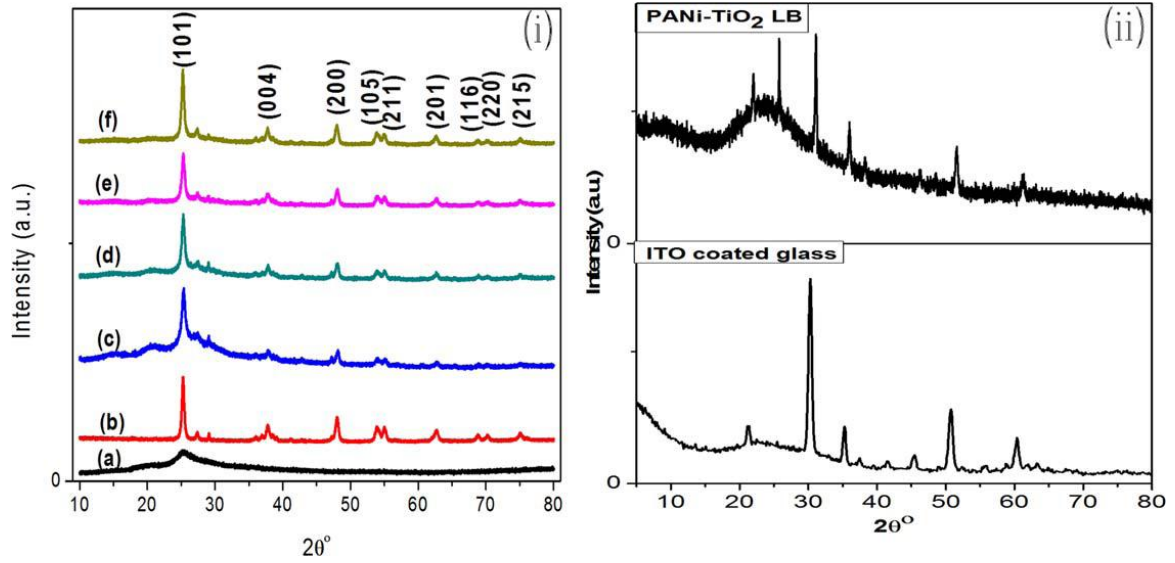


Figure 4.7: (i) XRD profile of (a) pure PANi, (b) TiO₂ nanoparticles, (c) 5, (d) 10, (e) 15, and (f) 20 wt % TiO₂ in PANi-TiO₂ nano-composite. (ii) XRD pattern of ITO-coated glass and LB film of 25 layers of PANi-TiO₂ (20 wt %) nano-composite.

Figure 4.7 show (i) XRD profile of (a) pure PANi, (b) TiO₂ nanoparticles, (c) 5, (d) 10, (e) 15 and (f) 20 wt % TiO₂ in PANi-TiO₂ nano-composite. (ii) XRD pattern of ITO-coated glass and LB film of 25 layers of PANi-TiO₂ (20 wt %) nano-composite deposited on ITO glass substrate. All peaks are in good agreement with the standard spectrum (JCPDS no.: 21-1272). XRD patterns for 5, 10, 15, 20 wt % TiO₂ in PANi-TiO₂ nano-composite, exhibiting diffraction peaks at $2\theta = 25.23^\circ, 37.73^\circ, 48.07^\circ, 53.86^\circ, 54.83^\circ, 62.59^\circ, 68.79^\circ, 70.15^\circ$ and 75.06° respectively. The hybrid component materials show the characteristics of both PANi and TiO₂. The broader peaks are due amorphous nature of PANi matrix. With increasing TiO₂ percentage in the composite, the intensity of the broad peak of PANi is decreased. The average particle size of PANi-TiO₂ (20 wt %) nano-composite is found to be 29 nm using Debye- Scherrer's equation,

$$\tau = K\lambda / \beta \cos\theta \quad (1)$$

where K is the shape factor, λ is wavelength of X-ray, β is the line broadening at half the maximum intensity (Full Width at Half Maximum) in radians, and θ is the Bragg's angle [37]. Figure 4.7(ii) shows X-ray diffraction patterns of the ITO coated glass substrate revealing peaks at $2\theta = 21.66^\circ, 30.52^\circ, 35.52^\circ, 37.68^\circ, 50.78^\circ$ and 60.72° (JCPDS Card No. 06-0416). They were assigned (211), (222), (400), (411), (440), and (622) diffraction peaks of ITO film [38, 39]. The XRD pattern of the LB film of 25 layers PANi-TiO₂ (20

wt %) nano-composite deposited ITO-coated glass, illustrated in Figure 4.7(ii), shows the peaks at $2\theta = 21.75^\circ$, 25.72° , 30.89° , 35.94° , 48.22° , 50.78° , and 62.59° . The peaks at $2\theta = 25.72^\circ$, 48.22° and 62.5° can be indexed to the anatase TiO_2 phase. The intensity of peaks of ITO at $2\theta = 21.75^\circ$, 30.89° , 35.94° , and 50.78° is dampened. The thickness of LB film of 25 layers is found to be 700 nm using Debye-Scherrer's equation.

4.6 Atomic Force Microscopy of PANi– TiO_2 Nano-composite LB Films

The PANi– TiO_2 nano-composite LB films were scanned under atomic force microscope (AFM) equipped with Silicon nitride (SiN) probe in noncontact mode. It has tip curvature radius 6 nm, attached to a cantilever having resonance frequency (87– 230 kHz), and force constant 5.1 N/m. The ITO coated glass substrate was initially scanned under AFM and root mean square (RMS) roughness ~ 1.4 nm was observed which ensures the smoothness of the substrate and its suitability for deposition of the monolayer.

4.6.1 Topography of PANi– TiO_2 Nano-composite LB Films

Figure 4.8(a) shows AFM image (512×512 pixels) of PANi– TiO_2 (20 wt %) nano-composites monolayer on the quartz substrate. Its corresponding height profile and its three dimensional (3D) view is shown in Figure 4.8 (b, c), respectively. Surface roughness average was 2.02 nm and RMS roughness was 2.67 nm. It is noted that the PANi– TiO_2 monolayer surface roughness is smooth at a molecular level and is composed of pebble-like protrusions. The monolayer microscopic structure is formed from nanometer-scale grains of TiO_2 surrounded by interconnected nanofibers network. We find maximum number of counts of particles having size ~ 29 nm as shown in Figure 4.8(d) [40]. Figure 4.8(e) shows the image of edge of the LB film of 25 layers of PANi– TiO_2 , scan range $2 \mu\text{m} \times 2 \mu\text{m}$. The height profile shows the approximate height is about 700 nm (along Z-axis) up to 1.2 mm then after that height profile reaches nearly zero indicating the surface of quartz as shown in Figure 4.8(f). Figure 4.8(g) shows 3D image of edge of the LB film of 25 monolayer of PANi– TiO_2 which also shows the height of LB film of 25 layers from above the quartz surface [25]. Figure 4.9 show non contact AFM Surface topography images scan rate 1Hz, scan range $5 \times 5 \mu\text{m}^2$ of a) 5%, (b) 10%, (c) 15%, (d) 20% wt of PANi– TiO_2 nano composite single monolayer LB films deposited on ITO coated glass substrate with an average height around 30nm. The increase in

concentration of nanoparticles also increases the orientation of host polymer matrix in LB films as observed in figure 4.8.

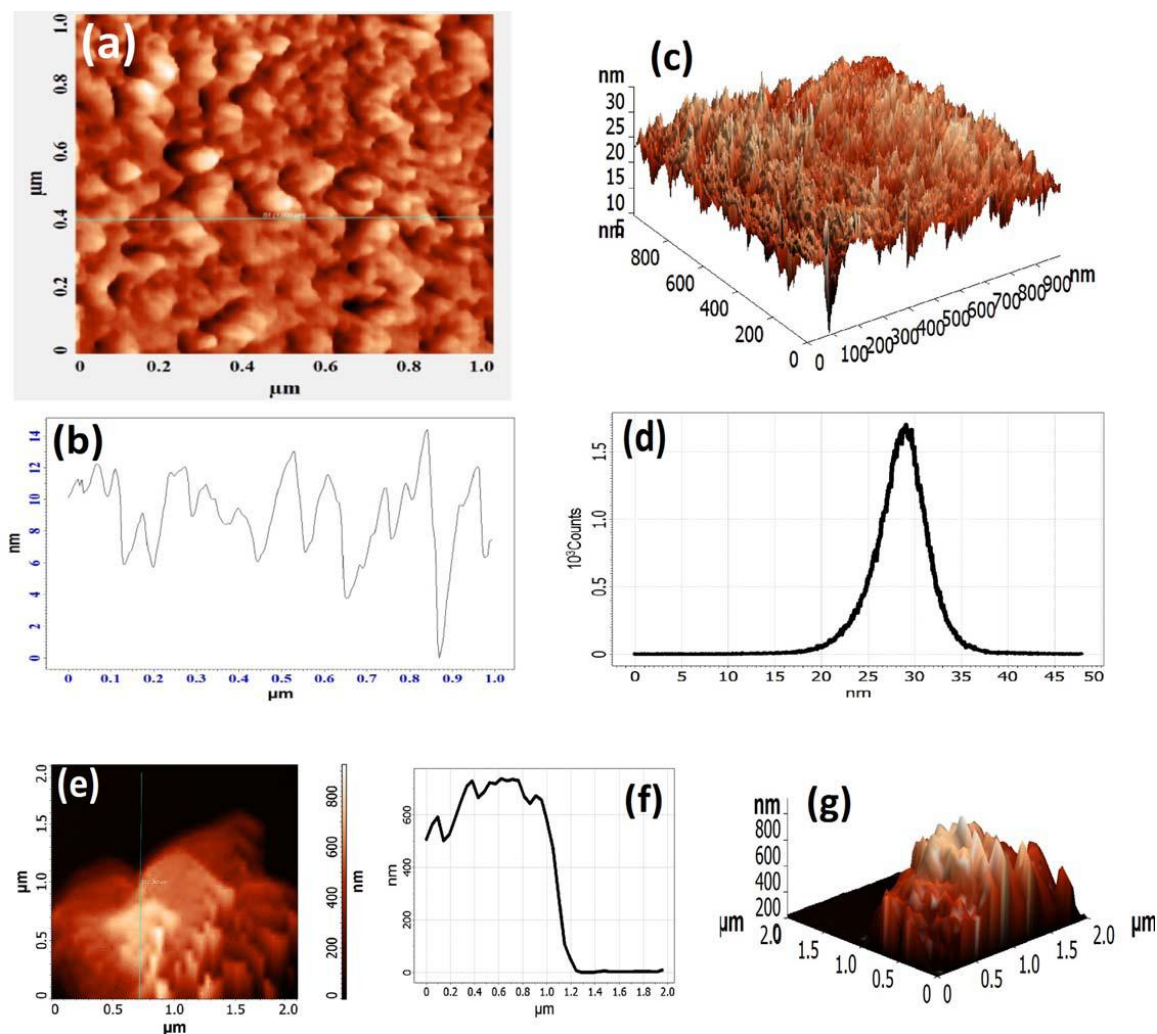


Figure 4.8: (a) AFM image of PANi-TiO₂ (20 wt %) nano-composite LB film deposited on the quartz substrate, (b) the corresponding height profile, (c) its 3D image and (d) count of particle size distribution, (e) AFM image of edge of LB film of 25 layers of PANi-TiO₂ (20 wt %) nano-composite, (f) the corresponding height profile and (g) 3D image.

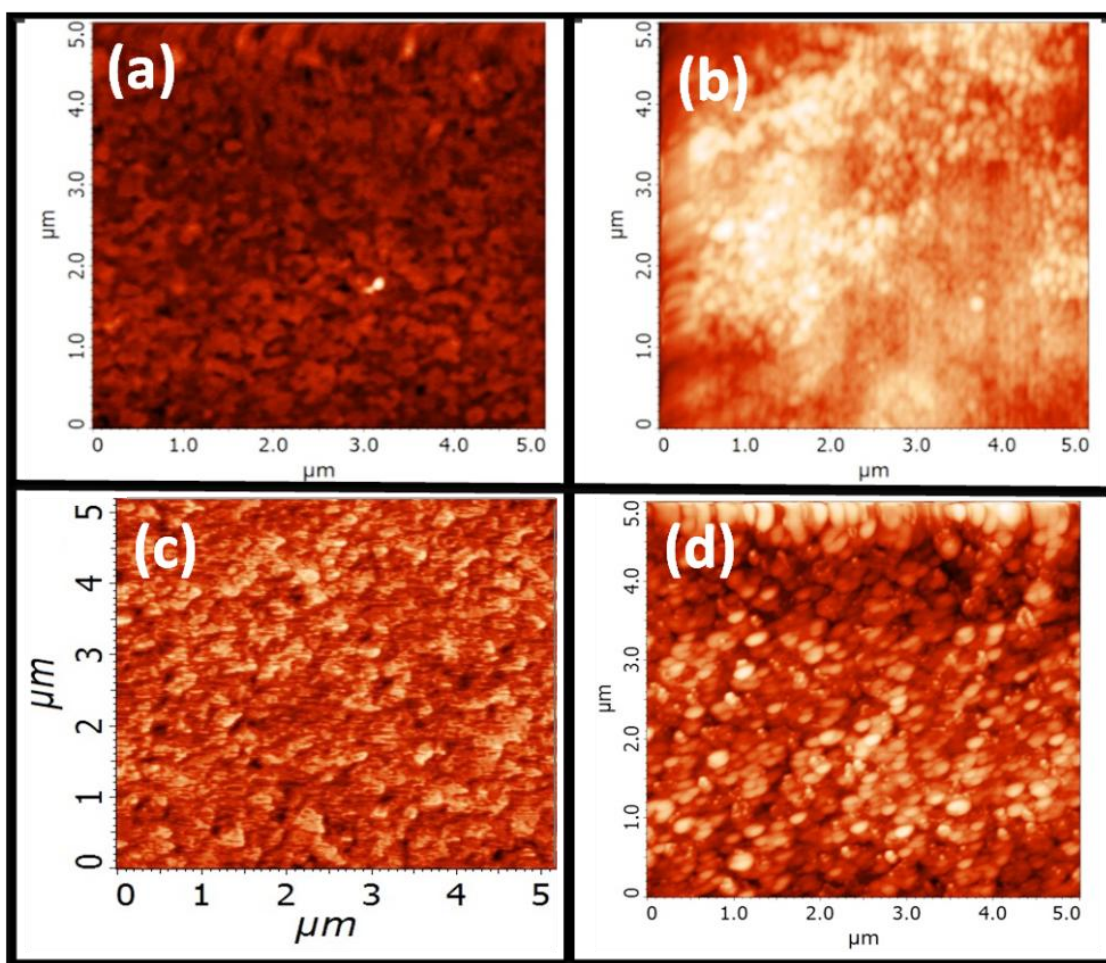


Figure 4.9: Surface topography images, scan range $5 \times 5 \mu\text{m}^2$ of a) 5, (b) 10, (c) 15, (d) 20 % wt of PANi-TiO₂ nano-composite single monolayer LB film in non contact AFM modes.

4.6.2 Phase Detection Microscopy (PDM)

Schematic picture for phase analysis of PANi (polymer)-TiO₂ nano-composite is shown in Figure 4.10. It shows clearly the soft elastic polymer as light bright region and hard nanoparticles as dark in colour.

Figure 4.11 shows a phase imaging of nano-composite Langmuir-Blodgett (LB) films containing a) PANi; (b) 5, (c) 10, (d) 15, (e) 20 weight percentages of TiO₂ in PANi.

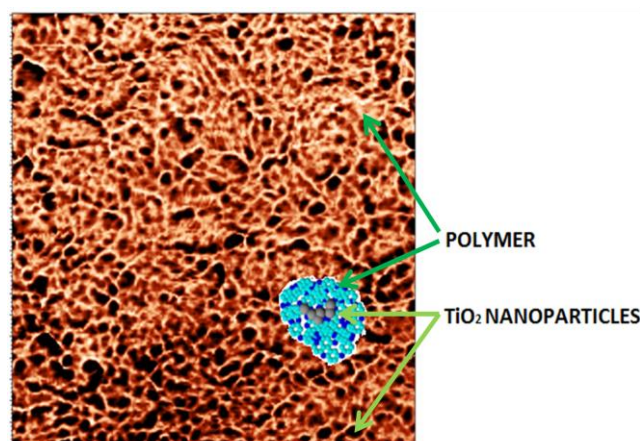


Figure 4.10: Schematic picture for phase analysis of PANi (polymer)–TiO₂ nano-composite.

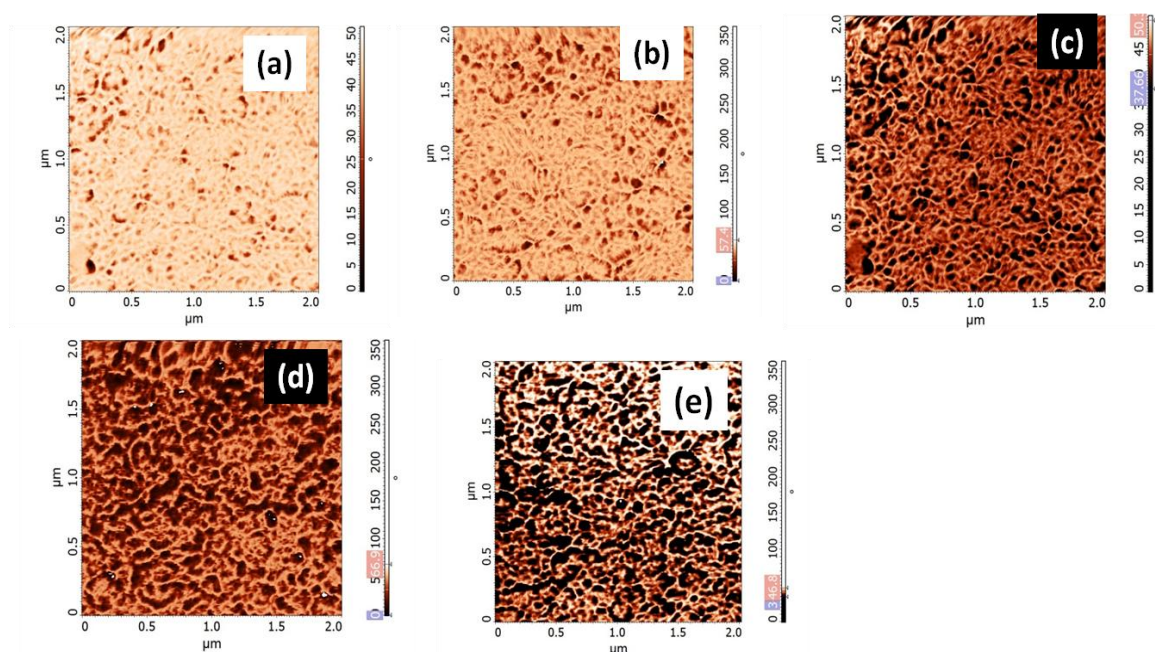


Figure 4.11: Phase imaging of nano-composite LB films containing a) PANi; (b) 5, (c) 10, (d) 15, (e) 20 weight percentages of TiO₂ in PANi.

Atomic force microscopy (AFM) Phase images of nano-composite Langmuir-Blodgett (LB) films containing a) PANi; (b) 5, (c) 10, (d) 15, (e) 20 weight percentages of TiO₂ in PANi reveal clearly the variations in the surface properties of the polymer with the increase in concentration of the TiO₂ nanoparticles in PANi monolayer. In Non-contact AFM phase imaging edges are highlighted and large-scale height difference do not affect the image, thus providing clearer view of fine features, which cannot be disclosed by rough topography. As seen in figure 4.11, upon increasing the amount of TiO₂ content in

the nano-composite, distortions in the network structure of polymer could be seen. The PANi morphology is interconnected nanofibers network with cross-sectional fibril dimensions of few nanometers. With the increase in concentration of TiO_2 in PANi, the density of connected paths decreases and the morphology appears foam-like with the PANi network surrounding the TiO_2 phase. This kind of morphology may be the cause of the higher electrical conductivities of the nano-composites.

Figure 4.12 shows AFM magnitude profile of $2 \times 2 \mu\text{m}^2$ (a) 5, (b) 10, (c) 15, (d) 20 wt % PANi- TiO_2 nano-composite recorded simultaneously with non contact height profiles and allows to distinguish areas with different friction which proves the surface is almost flat and LB films are uniformly deposited.

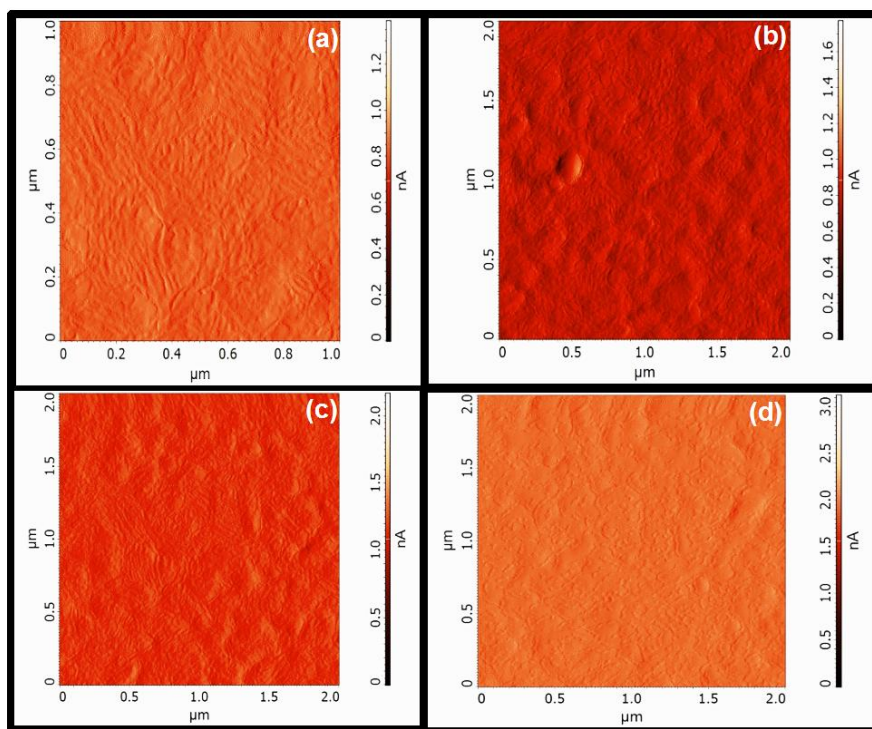


Figure 4.12: AFM magnitude profile of $2 \times 2 \mu\text{m}^2$ (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt % PANi- TiO_2 nano-composites.

4.6.3 Conductive Atomic Force Microscopy

For contact mode topography and conductivity measurements of the PANi-TiO₂ nano-composite LB films, a conductive (Pt-coated) cantilever (NT-MDT, CGS-01/Pt; frequency 4-17 kHz; force constant 0.03 N/m, curvature radius of the tip is 35 nm) is used. PTB certified Test grating TGQ1 -41680-09 (company NT-MDT) has been used to calibrate the AFM in X, Y and Z directions. Basic step height can vary from the specified one within $\pm 10\%$. The ITO coated glass was mounted on a special substrate (supplied with the Solver-NEXT) having a spring contact for conductivity analysis. The contacts on the film were provided by silver nano paint (SPI Ag Colloid). The topographical data was scanned in a grid of 512×512 pixels and scan size was $2 \times 2 \mu\text{m}^2$. Surface conductivity mapping has been obtained by operating the Scanning Probe Microscope (SPM) in conductive AFM (C-AFM) mode.

At a given voltage, the current measured by the instrument is given by the total circuit resistance, which is the sum of the resistance of the sample, tip and contact resistance between sample and the tip; the latter two resistances are assumed constant and negligible compared to the sample resistance. Once the scanning is complete, local I-V characteristic curves can be obtained by measuring the current at a selected point of the scanned area, with the variation of bias voltage applied in defined range (up to a maximum of -10V to +10V). With the cantilever tip of nanometer size, the local electrical properties in the nanoscopic level, can be probed by the I-V curves.

Figure 4.13 show atomic force microscopy images in contact mode $2 \times 2 \mu\text{m}^2$ (a) 5%, (b) 10%, (c) 15%, (d) 20% weight of TiO₂ in Polyaniline LB films on the ITO substrates; and their corresponding 3D images and the single-point current vs. voltage (I-V) curves corresponding to the points marked (in squares).

The average height of films is measured by the software NOVA P9 NTMDT (Image Analysis 2.1.0.800). Films of PANi-TiO₂ appear to be exhibiting interconnected nanofibers network kind of pattern surrounding the TiO₂ nanoparticles with an average

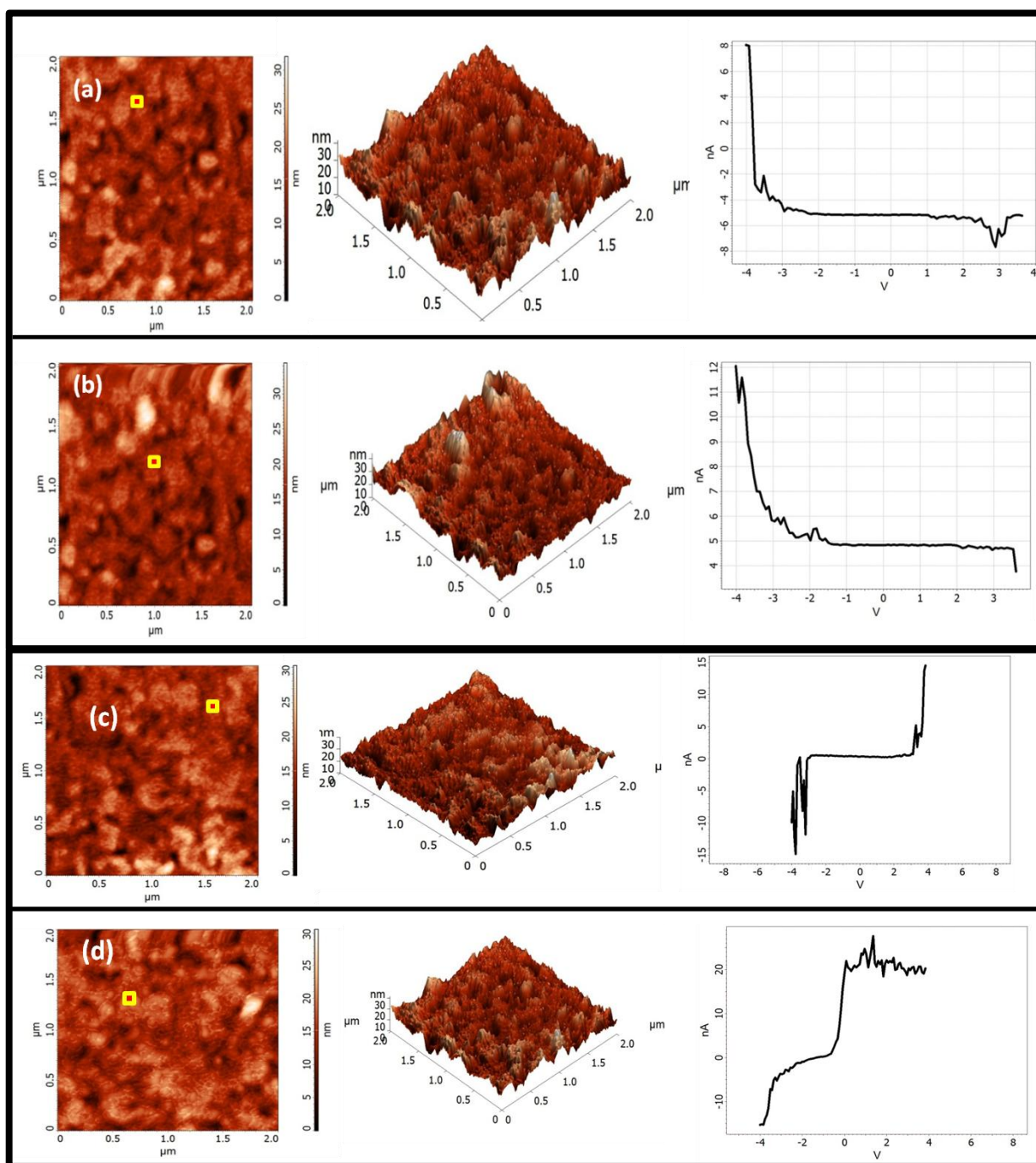


Figure 4.13: Atomic force microscopic height profile in contact mode $2 \times 2 \mu\text{m}^2$ (a) 5%, (b) 10%, (c) 15%, (d) 20% weight of TiO₂ in PANi; and their corresponding 3D images and Single-point electrical I–V characteristics corresponding to the positions (squares) marked on images (a-d).

height around 30nm. Examining the doping effect of TiO₂ on the thin film properties of PANi-TiO₂ nano-composites, it is observed that the topography did not change significantly. Because of the presence of molecular interactions such as hydrogen

bonding, polymers have the capacity of self-assemblage into hierarchical structures, so these polymeric nano-composites form nanoscale cylindrical structures.

The data presented is the result of single I-V measurements by software NOVA P9 NTMDT 2.1.0.800 and no averaging of curves has been performed. The I-V characteristics show currents ranging up to 8nA in 5%, 12nA in 10%, 14nA in 15% and 20 nA in 20 % PANi-TiO₂ nano-composite LB films [40]. The morphology of interconnected nanofibers network surrounding the TiO₂ may be the origin of the high electrical conductivities of the nano-composites. It indicates that for an increment of the dopant level there is increase in mobility of the charge carriers, which in turn is due to interchain interaction.

Figure 4.14 shows conductive data images of (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt % PANi-TiO₂ nano-composite LB film obtained with an applied bias voltage of 4V and are recorded simultaneously with topographical images [41]. Current distribution up to 8nA in 5%, 12nA in 10%, 14nA in 15% and 20 nA in 20 % PANi-TiO₂ nano-composite LB film is shown in Figure 4.14(a-d) and their corresponding 3D images respectively. The distribution of current on the whole surface of PANi LB film is almost uniform and almost homogeneous charge transport current have been observed in the surface conductance of the PANi-TiO₂ LB film. This shows the film is electrically homogeneous. The distribution of current on the surface of PANi-TiO₂ nano-composite LB films is almost uniform and very less charge transport current inhomogeneities have been observed in the surface conductance of the PANi-TiO₂ nano-composite LB film [42]. This is also indicated from the topography of PANi-TiO₂ nano-composite LB film in which the root mean square roughness as well as surface roughness average increases in comparison to PANi LB film.

4.7 Conclusions

The ultrathin self assembled films of PANi-TiO₂ nano-composites were prepared and characterized successfully. FTIR study shows the presence of both TiO₂ and PANi molecules in PANi-TiO₂ nano-composites, whereas XRD study confirmed the anatase phase and particle size of PANi-TiO₂. Electronic structure of PANi-TiO₂ and its LB film is confirmed by UV-Vis spectroscopy. The effect of doping the PANi with different concentration of TiO₂ nanoparticles on the surface pressure-area isotherms is observed which indicate an increase in condensed area of PANi-TiO₂ over PANi molecules at the air-water interface. The investigation revealed the inclusion of TiO₂ in the polymer

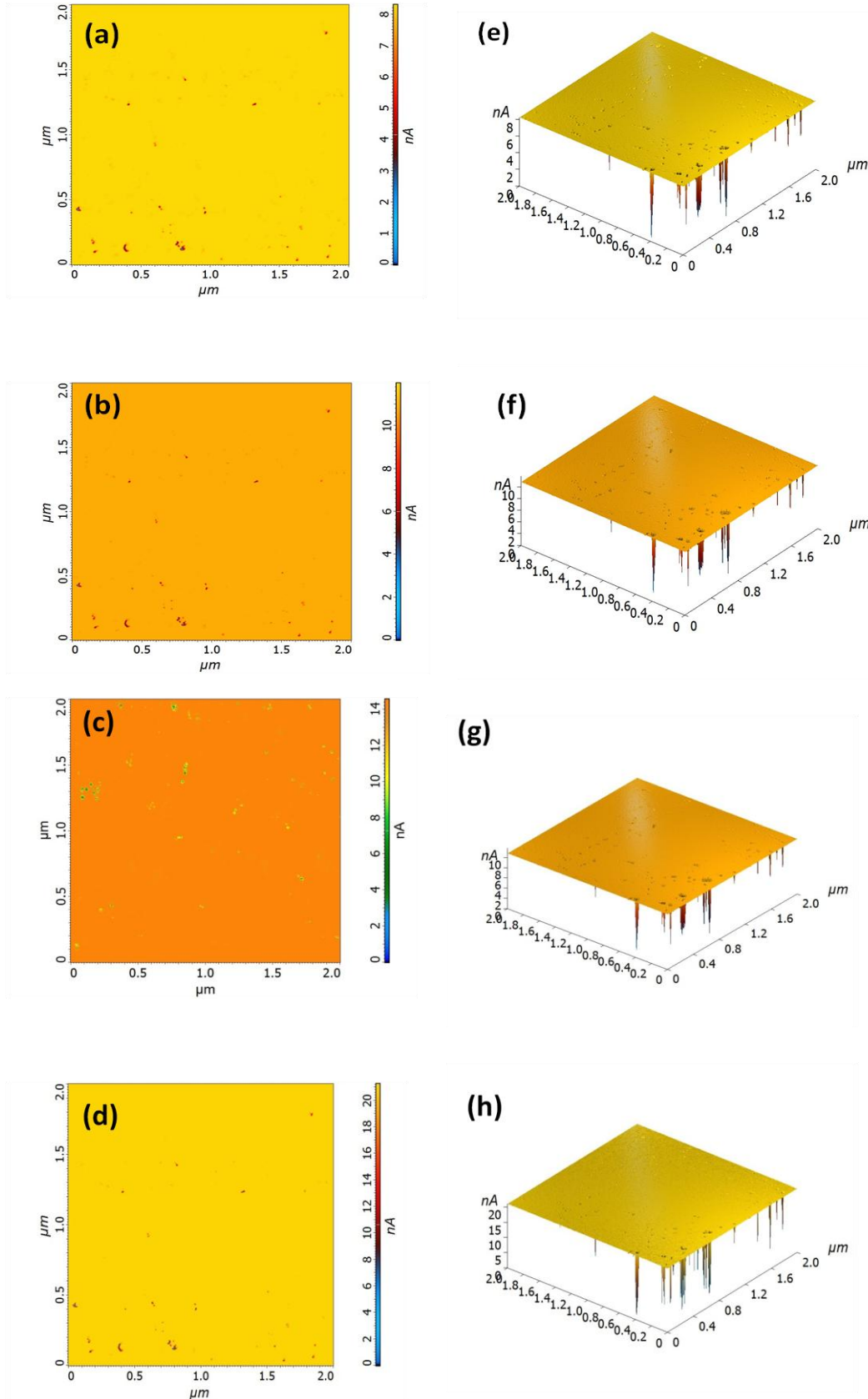


Figure 4.14: Conductive data images in Contact mode, scan range $2 \times 2 \mu\text{m}^2$ (a) 5%, (b) 10%, (c) 15%, (d) 20% weight of TiO_2 in PANi and (e-h) their corresponding 3D images, respectively.

matrix, which occurs during the film formation. Morphology of PANi–TiO₂ nano-composite LB films shows that they are formed from nanometer-size grains of TiO₂ surrounded by interconnected nanofibers network. Local Current-voltage (I-V) spectroscopy results show that there is increase in current range with increasing concentration of TiO₂ in nano-composite LB film. C–AFM data show almost uniform current distribution with increasing concentration of TiO₂ in nano-composite LB film. The possibility of manipulation of the material size and shape by LB technique is of great importance for a better use of conducting properties, thus extending its applications. This work is highly useful for sensor device fabrication technology and will also find applications in other organic–inorganic electronic devices.

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CHAPTER 5

Polyaniline-ZnO Langmuir-Blodgett Thin Films: Growth, Morphology, Optical and Electrical Characterization

Overview

Polyaniline–Zinc oxide (5, 10, 15, 20 weight %) materials were prepared by chemical route. Surface Pressure–Area (π -A) isotherms of PANi–ZnO show phase transformations of monolayer during the compression process. PANi–ZnO show good surface properties at air–water interface. Stable monolayers are formed at air–water interface which are efficiently transferred to solid substrate as ultrathin films by Langmuir–Blodgett technique. Thermal properties of Langmuir monolayers of PANi–ZnO nano-composite materials are studied at 10, 15, 20, 25, 30° C and electrical effects in monolayers are investigated by surface Potential and dipole moment measurements. UV-Visible spectroscopy revealed the modification of electronic structure of PANi with the addition of ZnO into PANi matrix. FTIR spectra provide information of the chemical bonding and show the shifting of absorption bands due to the bonding between ZnO nanoparticles and amine groups in the PANi molecular chains. XRD provide insights to the arrangement of heterogeneous films. The topography showed the presence of ZnO nanoparticles in the polymer chains. Local Current-voltage (I-V) spectroscopy results show that there is increase in current range in case of PANi-ZnO LB film as compared to PANi LB film. Conductive data images are recorded to probe charge transport current inhomogeneities in LB films and show almost uniform current distribution. These results would make them promising films for their applications in molecular nanoelectronic devices.

5.1 Introduction

In recent years polymer-inorganic composite materials have drawn attention due to their numerous potential applications in solar cells and other optoelectronic devices [1, 2]. In case of polymer-inorganic nano-materials, the surface to volume ratio of inorganic nano-materials is high which modify the electrical, optical and dielectric properties of the polymer and the use of inorganic nanoparticles into the polymer matrix provides high-performance novel materials that find applications in many electrical and electronics devices [3, 4]. Among inorganic nanoparticles, ZnO nanoparticles are of great interest due to their high surface energy, optical, electrical, catalytic, and electronic properties [5-10]. ZnO being noncentrosymmetric compound, find application in hybrid memories due to good resistance switching behavior [11-13].

The PANi-ZnO materials have been found to possess applications in sensors and other heterostructure devices [14-16]. The formation of ZnO-polyaniline also prevents the aggregation of nanoparticles [17, 18].

Langmuir Blodgett method is considered to be a viable means of producing ultrathin films with controlled film thickness and molecular packing [19]. The thickness of films deposited using the Langmuir–Blodgett technique is determined by the number of monolayers transferred to the substrate and can be precisely varied from a few nanometers to several microns [20]. It offers the possibility of constructing highly ordered systems, and the particular advantage in constructing composites is the intimate level of mixing at the molecular level. The electrical performance of organic materials is influenced by the molecular structure, molecular packing configuration and the long-range order [21].

Various composites of PANi with a number of transition metals, dopants have been synthesized, characterized and explored for various applications. However, very few reports are available regarding preparation and characterization of ultrathin films transition metal based PANi hybrid systems. This is one of the motivations behind investigating this work.

In this chapter, an attempt has been made to prepare and study structural, thermal, topographical and local electrical properties of PANi-ZnO Langmuir Blodgett thin films.

PANi-ZnO were analyzed by UV-Vis and FTIR spectroscopy and their LB films on indium tin oxide (ITO) coated glass substrates were analyzed by Atomic Force Microscopy (AFM), which furnishes 2D and 3D topological images. Electrical measurements were carried out by C-AFM in which a conductive probe is used to scan the sample in contact mode, while a DC bias is applied between the conducting tip and silver nano paint contact on ITO coated substrate. Current was recorded at a constant voltage as a function of position, for current mapping as well as current was recorded as a function of voltage at a specified sample position, for current–voltage (I–V) characterization [22]. Unlike other scanning probe-based techniques, C-AFM offers the possibilities of measuring simultaneously and independently topography and current maps of the samples at fixed voltage and enables to distinguish high and poor conductive regions [23-25].

5.2 Monolayer at air-water interface:

5.2.1 π -A isotherms:

The spreading solutions of PANi-ZnO (5, 10, 15, 20 wt %) were prepared in N-Methylpyrrolidone (NMP) by ultrasonication of the mixtures for 20 min. 200 microliter of the solution (particle concentration 0.125 mg/ml) was spread drop wise on the ultrapure Milli-Q₃ (pH=6.00) water subphase contained in trough by using Hamilton micro syringe separately. The area enclosed by the barriers (delrin) was reduced at the rate of 10 mm/min to compress the molecules on the water surface.

Langmuir films at the air-water interface were characterized for surface pressure-mean molecular area (π -A) isotherms to study alignment of molecules at air-water interface [26]. Figure 5.1 shows π -A isotherm profile of PANi–ZnO (5, 10, 15, 20 wt %) nano-composite materials at the air-water interface. Isotherms of all systems provide information regarding the configuration of the monolayer during its compression.

For spherical nanoparticles, the particles form a gas like phase at low densities, where the monolayer is highly compressible without significant increase in the surface pressure. As the monolayer is compressed, they start to form a condensed phase, usually a hexagonally close-packed structure due to the isotropic interparticle interactions. At this stage, the interparticle separation distance decreases with increased compression. This raises the possibility of obtaining a range of controllable properties that can be finely tuned without

extreme conditions such as high temperature and pressure. Isotherm profiles of PANi-ZnO (5, 10, 15, 20 wt %) indicate that at initial stage of compression, molecules were in gaseous phase (G), having no interaction among themselves. With the further compression of barriers, molecules come closer to each other, resulting in the formation of liquid expanded (L-E) phase of film which has limited degree of compression. Further reduction in area resulted in formation of condensed (S) phase and a stable monolayer at air-water interface which is incompressible [26]. Isotherms of PANi as explained in chapter 3 and PANi-ZnO systems have different behaviour which confirms that the presence of ZnO is affecting the orientation of polymer at interface [27].

The mean molecular area per molecule is found to increase with increasing concentration of ZnO nanoparticles and with increasing the target surface pressure. Isotherm shifts toward higher mean molecular areas which have been resulted due to formation of hexagonal close packed molecular structures on the sub phase and this is also supported by AFM topography.

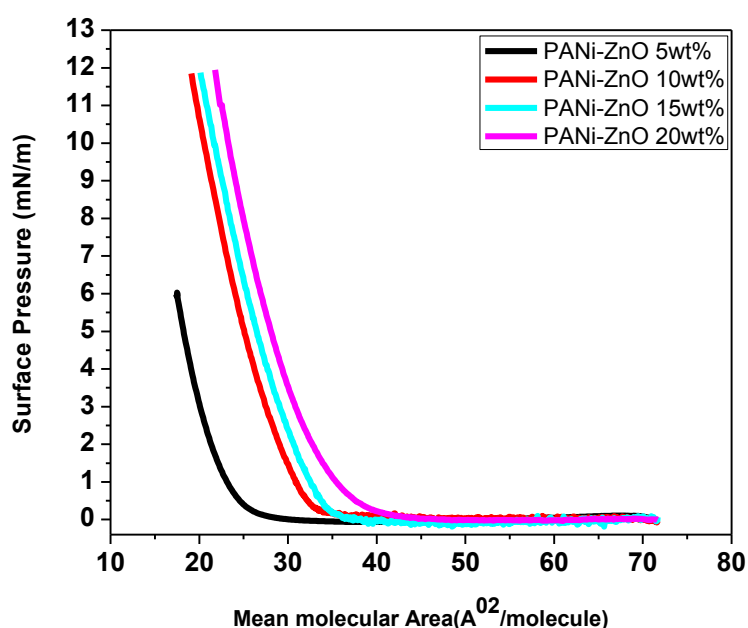


Figure 5.1: π -A isotherm profile of (5, 10, 15, 20) wt % PANi-ZnO monolayers; particle concentration 0.125 mg/mL in N-Methylpyrrolidone solution, spreading amount 200 μ L and compressed @ 10 mm/min.

At this composition (20 wt %) PANi and ZnO show better alignment on aqueous sub phase. So a packed network is formed due to the high surface energy of the nanoparticles, which is responsible for the decrease of free volume for the orientation of PANi chains. This results in higher surface pressure for 20 wt % system, due to molecular stability with nanoparticles [28].

The stability of the monolayer is monitored by holding the monolayer at the target pressure and observing the change in mean molecular area with time. When there is no change in mean molecular area and pressure with time then monolayer is considered stable and ready to transfer on solid substrate. Figure 5.2 show variation of surface pressure as a function of time at constant area for PANi-ZnO nano-composite molecules. It measures the stability of monolayer when barriers are in compressed state. An almost stable surface pressure with time (~ 1 hour) is attained at constant area per molecule.

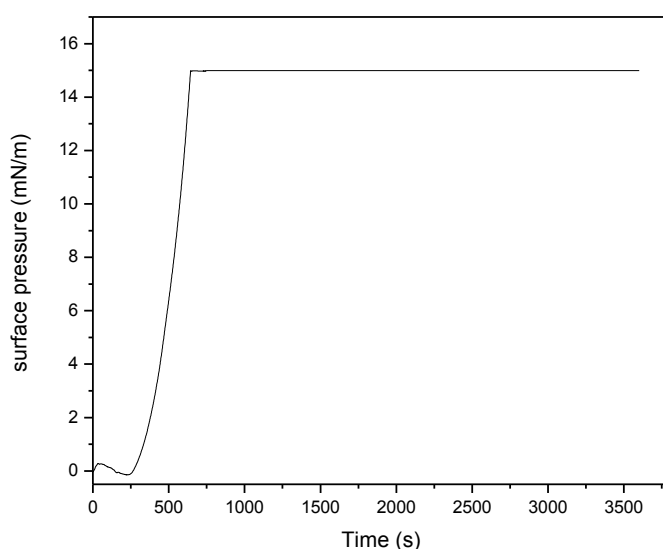


Figure 5.2: Surface pressure as a function of time at constant area shows that PANi-ZnO forms a stabilised layer at air–water interface at 15 m Nm^{-1} .

5.2.2 Hysteresis in π -A Isotherms

Three compression and expansion cycles were performed on monolayers of PANi-ZnO at the air–water interface to examine the reversibility and stability of the monolayer formation (Figure 5.3). With the increase in content of ZnO in nano-composite, hysteresis is observed during compression expansion cycles of barriers. This can be due to chain

entanglement of molecules and molecular reorganizations [29, 30]. The stability of monolayer is reduced with increase of concentration of ZnO nanoparticles.

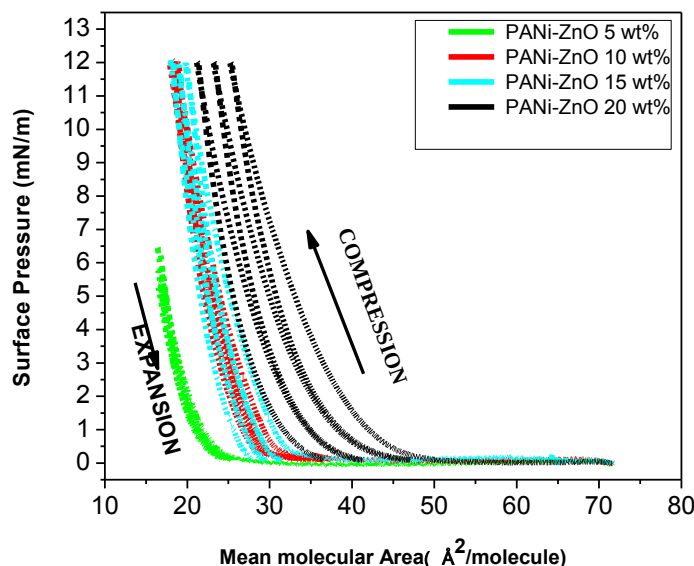


Figure 5.3: π -A multiple isotherms profile of PANi-ZnO (5, 10, 15, 20 wt %) nano-composite monolayer, particle concentration 0.2 mg/mL in NMP solution, spreading amount 200 μ L, target pressure 10 mN/m, rate 10 mm/min.

Figure 5.4 show π -A isotherm profiles of PANi-ZnO (20 wt %) nano-composite monolayer at various temperatures. Isotherm behavior is not much affected with the variation of temperature. There is slight increase in surface pressure with rise in temperature which may be due to the change in surface tension of subphase water with variation of temperature without affecting the stability of film.

The monolayers were deposited on Indium tin oxide (ITO) coated glass substrates at a constant surface pressure by vertical dipping method and the dipping speed was 2.0 mm/min [31]. Density, thickness and homogeneity properties were preserved while transferring the Langmuir film onto the substrate. The molecules in their solid phase are removed from the surface of water by suitably raising the substrate from water and the Z-type LB film is built up with transfer ratio 1.01 which indicates good transfer of molecules to the substrate [27]. The deposited films were dried in vacuum dessicator to ensure moisture free environment [32].

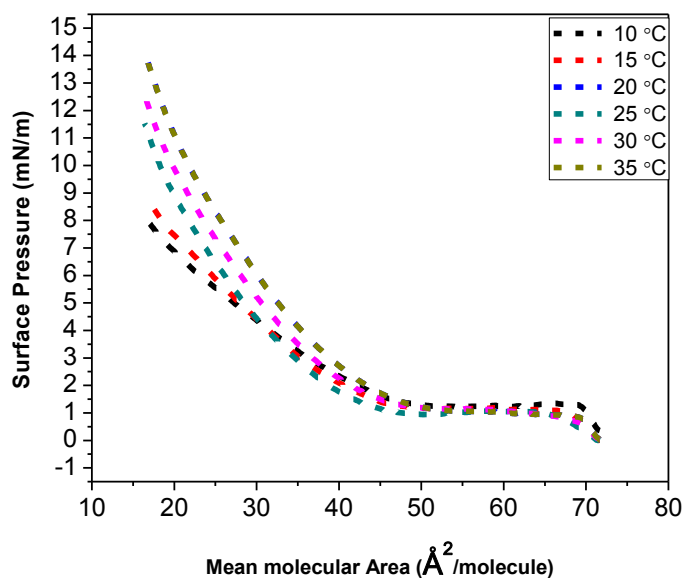


Figure 5.4: π -A isotherm profile of PANi-ZnO monolayer at various temperatures.

5.2.3 Electrical Effects in Monolayers:

5.2.3.1 Surface Potential investigations for PANi-ZnO Langmuir monolayers at Various Temperatures

To explore the surface potential isotherms, temperature of sub-phase was maintained at 10° , 15° , 20° , 25° , 30° C. by Julabo bath circulator. Figure 5.5 show surface potential as a function of Mean molecular area at temperatures 10° , 15° , 20° , 25° , 30° C for 20 wt % PANi-ZnO nano-composite. Even the small change in the molecular arrangement with temperature is detected by measuring the change in surface potential.

In case of molecules with short alkyl chain surface pressure increases with increase in temperature because π -A isotherm is dominated by the interaction between the hydrophilic part and the aqueous surface. Surface potential increases with increase in temperature. Non-zero surface potential is observed in ΔV -A isotherms indicating the existence of molecular domains even at large areas per molecule. With the compression these domains come closer. As compared to the fluctuations in ΔV -A isotherms at lower temperatures (10 - 25° C), a stable ΔV -A isotherm is seen for temperature 30° C.

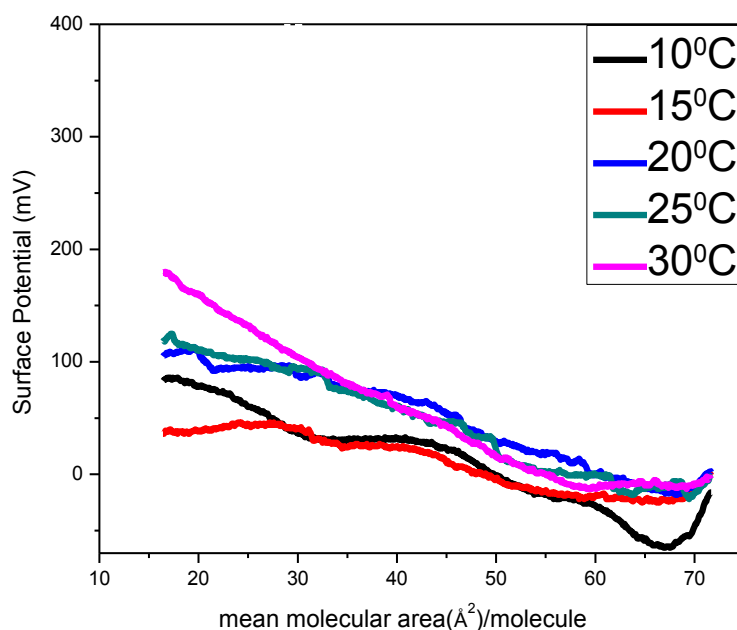


Figure 5.5: Surface Potential as a function of Mean molecular area at temperatures 10⁰, 15⁰, 20⁰, 25⁰, 30⁰ C.

5.2.3.2 Dipole moments for PANi-ZnO Langmuir monolayers at Various Temperatures

Dipole moment is calculated by using Helmholtz equation given in chapter 3 (eqn 2) and dipole moment profile is shown in figure 5.6 Domains become compact at higher temperature and resulted in increase of dipole moment values [33].

A π - π stacking attractive force is formed between molecules. The temperature-dependent properties of lattice arrangement of molecule are regulated by intermolecular forces as well as its interaction with the water surface. The domains become more compact with rising temperature indicating the dominance of dipolar interactions at the lower temperatures. Hence, the normal dipole moment appears to increase with increasing temperature [34].

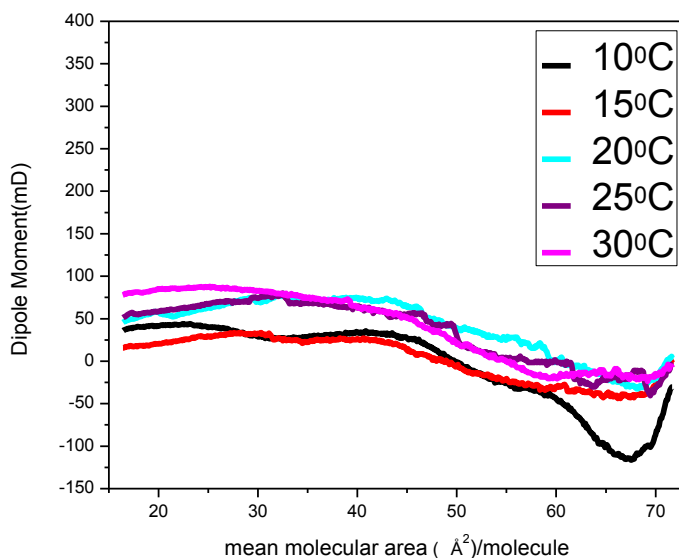


Figure 5.6: Dipole moment as a function of mean molecular area.at temperatures 10⁰, 15⁰, 20⁰, 25⁰, 30⁰ C.

5.3 Electron Absorption Spectroscopy of PANi-ZnO nano-composites

Figure 5.7 shows spectra of ZnO nanoparticles and (5, 10, 15, 20 wt %) PANi-ZnO in N-Methylpyrrolidone (NMP) using UV-visible spectrophotometer (Analytic Jena, SPECTROD 205). It indicates that pure ZnO absorb light of wavelengths below 400 nm (UV region) only and PANi-ZnO has broad absorbance in the UV and visible regions. All of the characteristic peaks of ZnO and PANi appear in PANi-ZnO nano-composites, but there is one more peak at 465 nm. So the three characteristic bands of PANi-ZnO composite appear at 320 nm, 465 nm and 635 nm, which can be attributed to the π - π^* , polaron- π^* and π -polaron transition respectively [35]. The presence of broad absorption band extended towards near infrared is indicative of charge carrier de-localization in the polaron band favoured by an expanded chain conformation of the PANi. The de-localization is responsible for the creation of polaron structure of polyaniline and significant increase of conductivity [36].

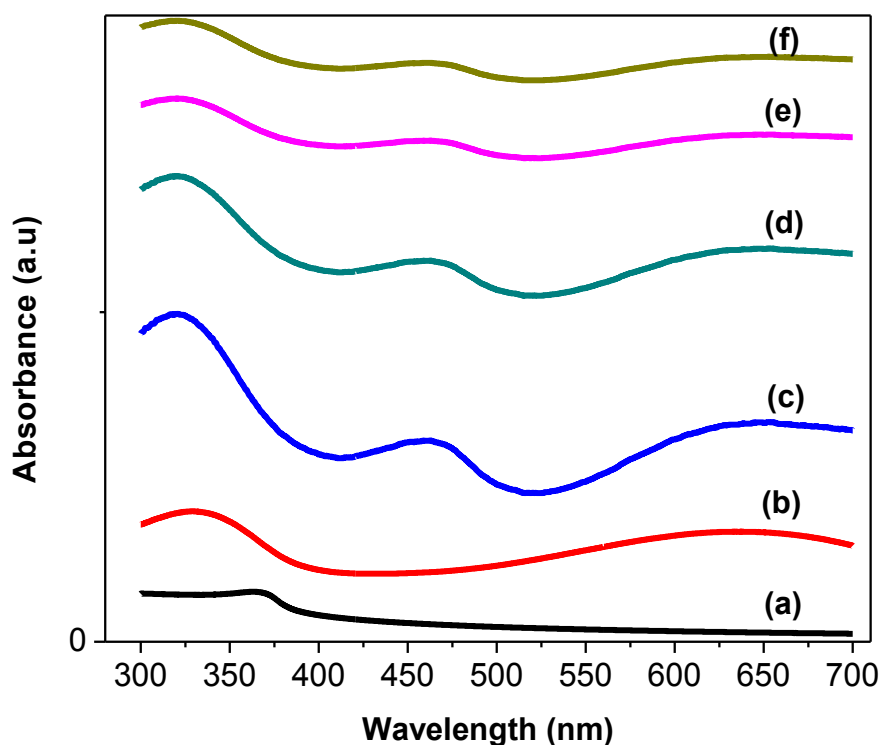


Figure 5.7: UV-visible spectra of the (a) ZnO nanoparticles, (b) PANi, (c) 5, (d) 10, (e) 15 (f) 20wt % ZnO in PANi-ZnO nano-composite, respectively.

5.4 Fourier transform infrared spectroscopy of PANi and PANi-ZnO nano-composites

FTIR spectroscopy profile of PANi, ZnO nanoparticles, and (5, 10, 15, 20 wt %) PANi-ZnO is shown in Fig. 5.8. The measurements were carried out by FTIR spectroscope (BX-II, Perkin Elmer), resolution 4 cm^{-1} and no. of scans 16; scan range 400 to 4000 cm^{-1} at room temperature. The main characteristic bands of pure PANi are explained in detail in chapter 1. 5.8(b) depict the broad band in the range of $3350\text{--}3500\text{ cm}^{-1}$ which is associated to the adsorbed H_2O molecule whereas, the absorption band at 501 cm^{-1} is the stretching mode of ZnO. The other peaks seen at 1382 cm^{-1} and 2353 cm^{-1} are observed may due to the carbonate components as the FTIR measurements were carried out in air [37].

The peaks for PANi-ZnO 5 wt % (figure 5.8c) appears at 1561 cm^{-1} (C=C stretching mode of the quinoid rings), 1476 cm^{-1} (C=C stretching mode of benzenoid rings), 1286 cm^{-1} (C-N stretching mode) and 1103 cm^{-1} (quinoid ring), indicating the formation of

PANi in the composite. It was observed that in comparison to PANi, the IR spectra of (5, 10, 15, 20 wt %) PANi-ZnO showed a red shift (lower wave-number) and hence indicating the weakened bond strengths and the conjugated system of PANi and increased density of electrons in ZnO, thus improved photocatalytic activity of PANi-ZnO nano-composites. The absorption bands shifts are due to the hydrogen bonding between the hydroxyl groups on the surface of ZnO nanoparticles and the amine groups in the PANi molecular chains [27, 38, 39].

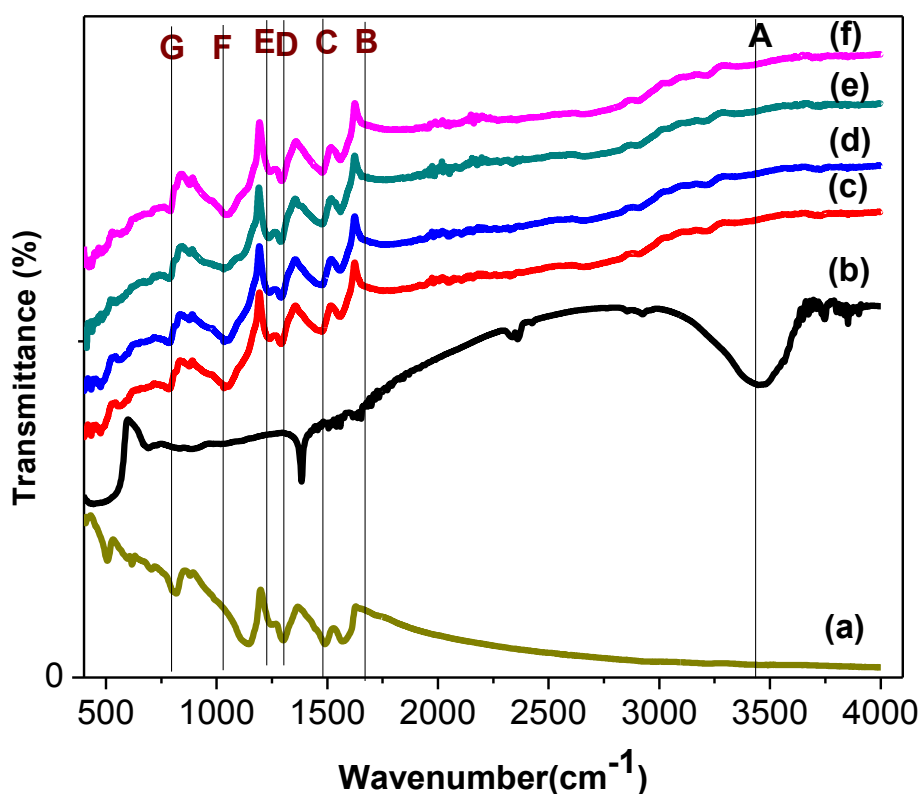


Figure 5.8: FTIR profile of the (a) PANi, (b) ZnO nanoparticles, (c) 5 wt %, (d) 10 wt %, (e) 15 wt %, (f) 20 wt % ZnO in PANi-ZnO nano-composite.

The comparison and significance of various peaks acquired by IR spectra of PANi and (5, 10, 15, 20 wt %) PANi-ZnO are given in Table 5.1.

Table 5.1: Peaks acquired by FTIR spectra of PANi and (5, 10, 15, 20 wt %) PANi-ZnO and their significance.

FTIR Peaks (cm ⁻¹)						
S. No.	PANi	PANi-ZnO				Significance
		5wt %	10wt %	15wt %	20wt %	
A	3445	3220	3220	3219	3213	N-H stretching
B	1565	1561	1559	1558	1557	C=C Quinone
C	1469	1467	1467	1467	1466	C=C Benzene
D	1299	1286	1286	1285`	1283	C=N Quinone
E	1245	1237	1229	1229	1223	C=N Benzene
F	1145	1104	1048	1048	1048	Aromatic C-H in plane bending
G	826	792	788	788	788	Aromatic C-H out of plane Benzene

5.5 X-ray Diffraction of ZnO nanoparticles and PANi-ZnO nanocomposites

X-Ray diffraction profile of ZnO nano particles is shown in figure 5.9 (b). The characteristic peaks were obtained at $2\theta = 31.72^\circ$, 34.50° , 36.30° , 47.75° , 56.60° , 63.10° and 68.00° corresponding to the miller indices (100) (002) (101) (102) (110) (103) and (201), respectively. The lattice constants $a = b = 3.2257 \text{ \AA}$ and $c = 5.2547 \text{ \AA}$ were obtained as using powder XRD software. The diffraction peaks are in good agreement with JCPDS cards (card no. 36-1451, $a = b = 3.249 \text{ \AA}$, $c = 5.206 \text{ \AA}$).

ZnO exhibits hexagonal close packed wurtzite structure as also shown in figure 5.10 [40]. The (002) plane lies parallel to the planes having alternating O and Zn atoms layers and (100) plane intersects it lying perpendicular to (002) plane [41, 42].

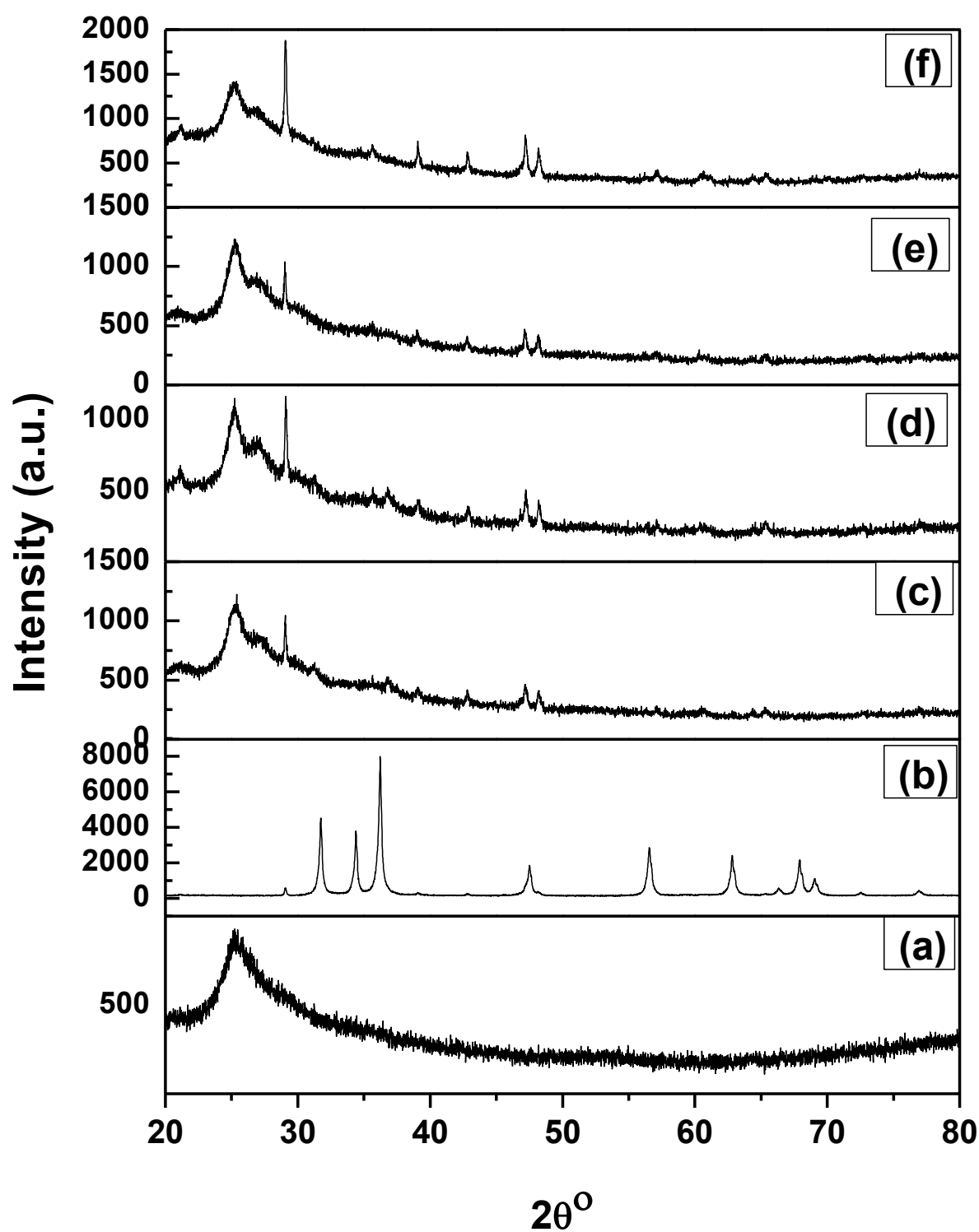


Figure 5.9: XRD profile of (a) pure PANi, (b) ZnO nanoparticles, (c) 5, (d) 10, (e) 15, and (f) 20 wt % ZnO in PANi–ZnO nano-composites.

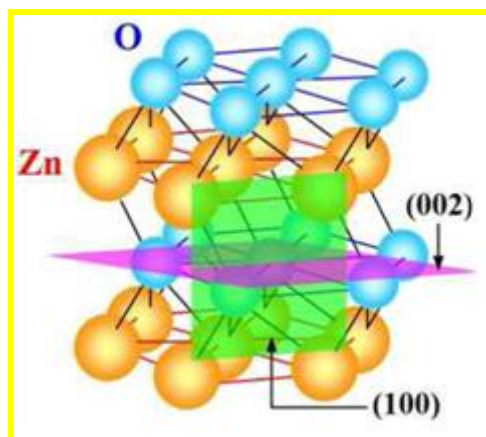


Figure 5.10: ZnO hexagonal-close-packed wurtzite structure showing the ZnO lattice [40].

The average particle size is found to be ~ 50 nm, calculated using Debye-Scherrer's equation

$$\tau = K\lambda/\beta\cos\theta \quad (2)$$

where K is the shape factor, λ wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg's angle.

X-Ray Diffraction pattern of PANi and (5, 10, 15, 20 wt %) PANi-ZnO nano-composites LB films of 26 monolayers deposited on ITO coated glass substrate is shown in figure 5.9. The XRD pattern of PANi as reported in chapter 1 show a broad peak was at $2\theta = 25^\circ$ showing the amorphous nature. The hybrid component materials show the characteristics of both PANi and ZnO. In the nano-composite, the intensity of the peaks is decreased as compared to that of ZnO.

The lattice parameters of nano-composite obtained from XRD peaks are $a = b = 3.245$ Å, $c = 5.207$ Å.

The structure of PANi-ZnO nano-composite has improved from amorphous to crystalline, as in pure PANi only one broad hump at $2\theta = 25^\circ$ is observed, while in case of PANi nano-composite peaks of ZnO are appearing with significant shifts. The hump at 25° in pure PANi becomes narrower in nano-composite showing the dominance of crystalline structure [43].

It is observed from figure 5.9 that the intensity of the peaks was increased by increasing concentration of ZnO nanoparticles indicating an interaction of ZnO nanoparticles and PANi due to hydrogen bonding between H-N and oxygen atoms of ZnO [44].

5.6 Atomic Force Microscopy of PANi-ZnO LB films

Topography and conductivity measurements of the PANi-ZnO LB films were performed using AFM (Solver-NEXT NT-MDT, Zelenograd, Moscow, Russia) equipped with Silicon nitride (SiN) probe in noncontact mode. The probe has tip curvature radius 6 nm, attached to a cantilever having resonance frequency (87–230 kHz), and force constant 5.1 N/m. Contact mode topography and conductivity measurements of the PANi-Zno nano-composite LB films were performed using a conductive (Pt-coated) cantilever (NT-MDT, CGS-01/Pt; frequency 4-17 kHz; force constant 0.03 mN/m, curvature radius of the tip is 35 nm). PTB certified Test grating TGQ1 -41680-09 (company NT-MDT) are used to calibrate the AFM in X, Y and Z directions. Basic step height can vary from the specified one within $\pm 10\%$. The LB film on the ITO substrate was mounted on a special substrate (supplied with the Solver-NEXT) having a spring contact for conductivity analysis. The contacts on the film were provided by silver nano paint (SPI Ag Colloid). The topograpcal data was scanned in a grid of 512×512 pixels and scan rate was 1 Hz. The average height is measured by the software NOVA P9 NTMDT (Image Analysis 2.1.0.800). The films were dried in vacuum desicators before imaging.

5.6.1 Topography of PANi-ZnO nano-composites LB films in Non - contact mode

Figure 5.11 show non contact AFM height profiles of a) 5%, (b) 10%, (c) 15%, (d) 20% wt of PANi-ZnO nano-composite single monolayer LB films deposited on ITO coated glass substrates and their corresponding three-dimensional (3D) topography images. Scan rate is 1Hz Figure 5.11(a-d) shows that the average height of PANi-ZnO LB films is 60 nm which ensures that the ZnO nano-particles of size 50 nm are embedded in the polymer [45]. Due to the restrictions of polymeric network around ZnO, the resulting morphology is mainly disordered.

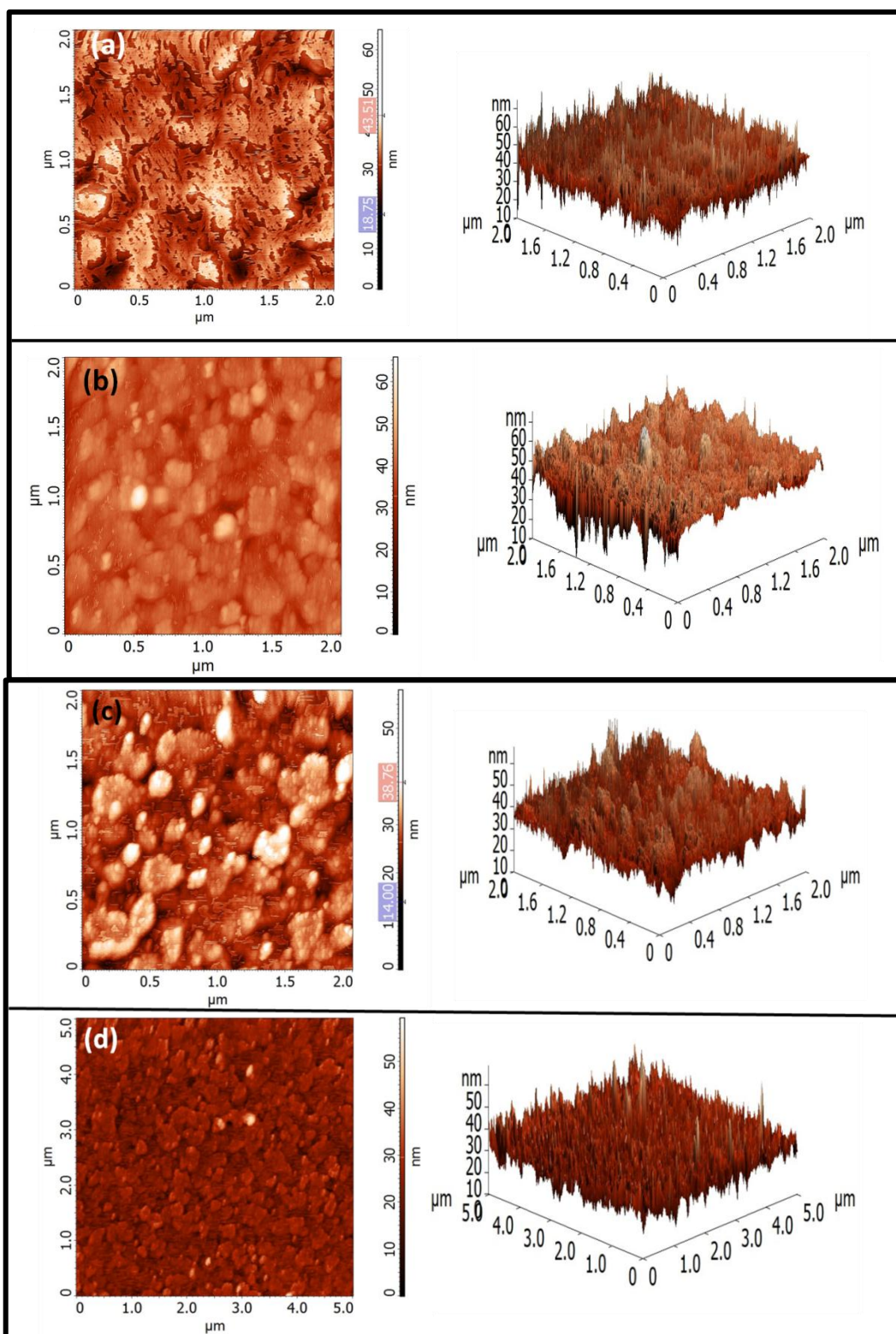


Figure 5.11: Non contact AFM height profiles of a) 5%, (b) 10%, (c) 15%, (d) 20% wt of PANi-ZnO nano composite single monolayer LB films mode and their corresponding 3D images.

5.6.2 Phase Imaging

Figure 5.12 shows a phase imaging of nano composite Langmuir-Blodgett (LB) films containing a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt % of ZnO in PANi. Atomic force microscopy Phase images of nano composite Langmuir-Blodgett (LB) films reveal clearly the variations in the topography of the PANi with the increase in concentration of the ZnO nanoparticles. Figure 5.12 shows the interconnected polymer networks that wrap the nanoparticles. The PANi-ZnO networks undergo a nano phase separation. Due to the restrictions of the network of PANi the resulting morphology is mainly disordered.

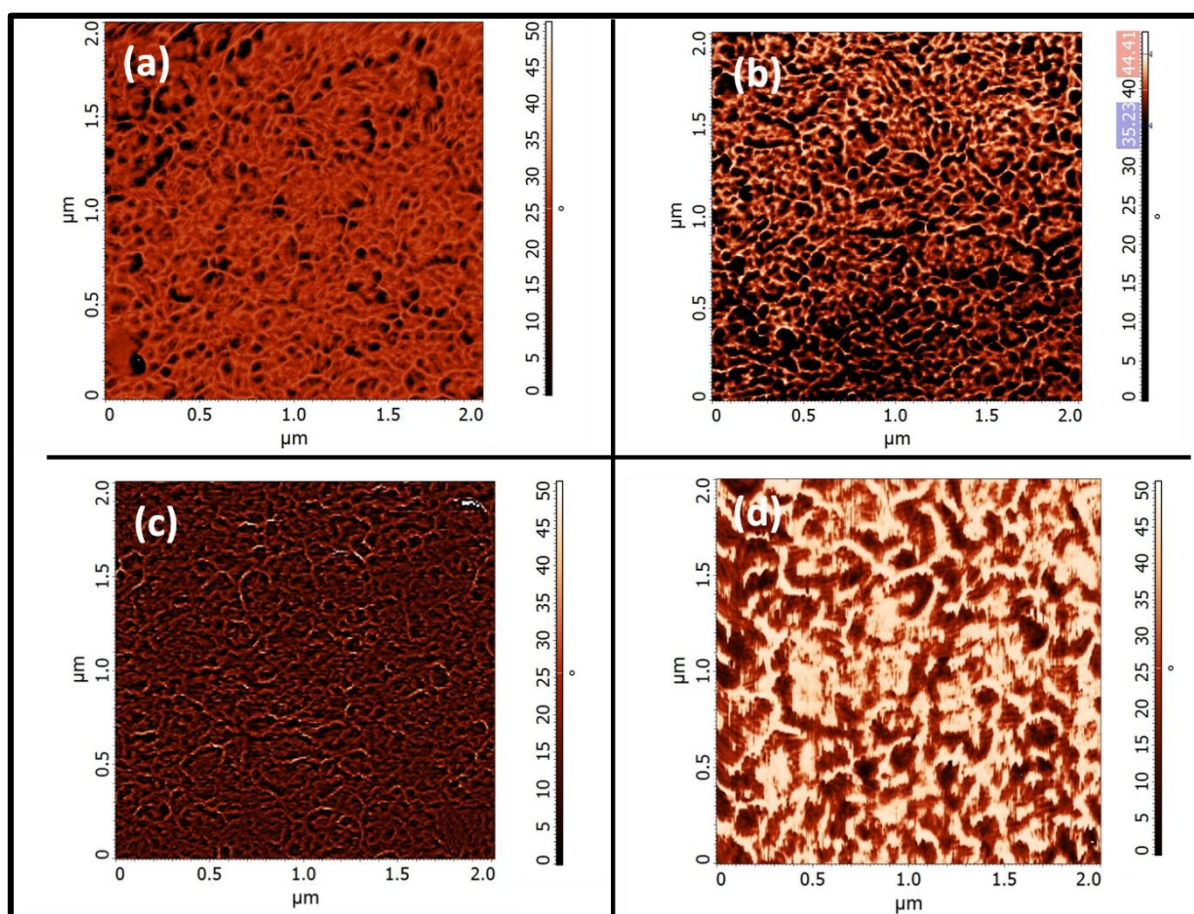


Figure 5.12: Phase imaging of nano composite LB films containing a) 5%, (b) 10%, (c) 15%, (d) 20% weight percentages of ZnO in PANi.

The AFM images reveal higher density of hexagonal close packed wurtzite ZnO nanoparticles with increase in concentration of the ZnO nanoparticles in PANi- ZnO nano-composite LB film. Such increase in the density may results in reduction in energy gap of the LB films of the nano-composites.

Phase image for the nano-composite films; show a polymer-rich surface. With the increase ZnO nanoparticles, nano-composite films show a ZnO nanoparticles-rich surface with more ZnO nanoparticles exposed on the surface [46].

Figure 5.13 show AFM magnitude profile of $2 \times 2 \mu\text{m}^2$ (a) 5%, (b) 10%, (c) 15%, (d) 20 wt % PANi–ZnO nano-composite LB films recorded simultaneously with non contact height profiles and allows to distinguish areas with different friction which proves the surface is almost flat and LB films are uniformly deposited.

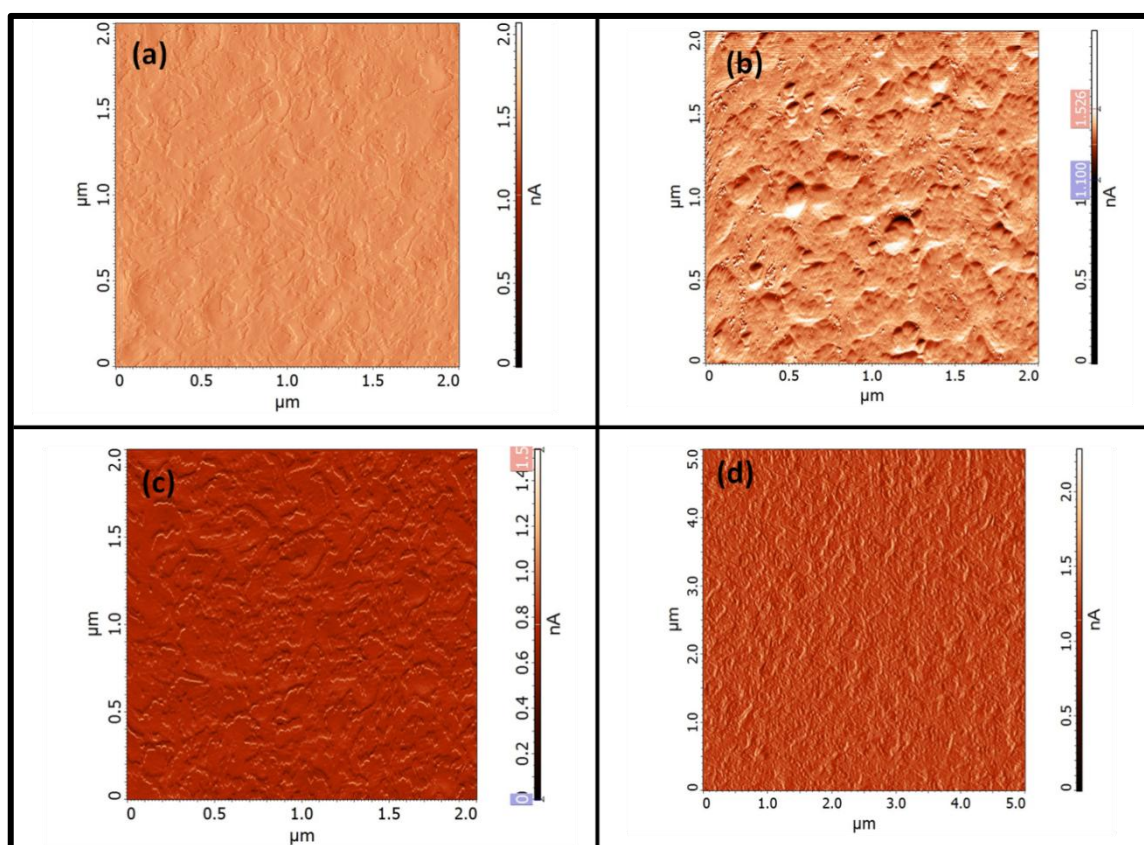


Figure 5.13: AFM magnitude profile of $2 \times 2 \mu\text{m}^2$ (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt % PANi–ZnO nano-composite LB films.

5.6.3 Conductive Atomic Force Microscopy

Surface conductivity mapping has been obtained by operating the Scanning Probe Microscope (SPM) in conductive AFM (C-AFM) mode.

At a given voltage, the current measured by the instrument is given by the total circuit resistance, which is the sum of the resistance of the sample, tip and contact between the sample and the tip; the latter two resistances can be usually considered constant and

negligible compared to the sample resistance. Once the scanning is complete, local I-V characteristic curves can be obtained by measuring the current at a selected point of the scanned area, by varying applied bias voltage in a defined range (up to a maximum of -10V to +10V). With the cantilever tip of few nm² size, the local electrical properties in the nanoscopic level, can be probed by the I-V curves.

Figure 5.14 show atomic force microscopy images in contact mode 2 × 2 μm² (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt % of ZnO in PANi LB films on the ITO substrates; and their corresponding 3D images and the single-point current vs. voltage (I-V) curves corresponding to the points marked (in squares).

The average height of films is measured by the software NOVA P9 NTMDT (Image Analysis 2.1.0.800). The average height of PANi-ZnO LB films is 60 nm. This is much more than the 25 nm for PANi LB film as discussed in chapter. This hints that the ZnO nanoparticles (of size 50 nm) are embedded in the polymer chains and are deposited uniformly. The average molecular length of monomer of PANi as reported in earlier is very small (~ 5 Å) [26] and the polymerization mechanism of aniline on the surface of ZnO nanoparticles show increase in average height of PANi-ZnO LB film as compared to that of PANi and ZnO nanoparticles. Analyzing the effect of doping of ZnO on the thin film of PANi-ZnO nano-composites, it is observed that the topography, measured by atomic force microscopy (AFM) on ITO glass substrates, change significantly with root mean square roughness, R_q values between 2.8 and 4.5 nm. LB films show the change in the root mean square roughness, R_q and surface roughness, R_a upon the introduction of ZnO nanoparticles into the PANi matrix. The comparison of root mean square roughness, R_q and surface roughness average, R_a for (5, 10, 15, 20 wt %) PANi-ZnO nano-composite LB films are given in Table 5.2. Moreover, with the increase of ZnO nanoparticle's concentration into the PANi matrix, the root mean square roughness and surface roughness average of the nano-composite has increased and this confirms the morphological change in the nano-composite. This again conveys the same information as given by phase changes of isotherms. The 3D view of the AFM of PANi-ZnO LB films exhibited a mountain valley kind pattern.

Table 5.2: The comparison of root mean square roughness, R_q and surface roughness average of PANi-ZnO nano-composite LB films.

Samples	Area	Surface roughness Root mean square average, R_a (nm)	roughness, R_q (nm)
5 wt % PANi-ZnO	$2 \times 2 \mu\text{m}^2$	2.2	2.8
10 wt % PANi-ZnO	$2 \times 2 \mu\text{m}^2$	2.8	3.7
15 wt % PANi-ZnO	$2 \times 2 \mu\text{m}^2$	3.1	3.9
20 wt % PANi-ZnO	$2 \times 2 \mu\text{m}^2$	3.4	4.5

Size of nano-composites LB films determined by XRD technique also match the average height of morphology seen by AFM. The organization of the spherical ZnO nanoparticles leads to hexagonal close packed structure due to isotropic interparticle interactions [44]. π electrons of benzoid /quoinoid rings form π - π stacking with π electrons of oxygen of ZnO hexagonal closed-packed wurtzite structure. This π - π stacking interaction is an important aspect in molecular self-assembly technique. This aromatic stacking interaction phenomenon, affects aromatic polymer and ZnO groups.

The data presented is the result of single I-V measurements by software NOVA P9 NTMDT 2.1.0.800 and no averaging of curves has been performed. The I-V characteristics show currents ranging up to 8nA in 5%, 12nA in 10%, 14nA in 15% and 20 nA in 20 % PANi-ZnO LB films [27, 47].

Figure 5.15 show conductive data images of (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt % PANi-ZnO nano-composites LB films obtained with an applied bias voltage of 4V and are recorded simultaneously with topographical images [48]. Current distribution up to 10nA

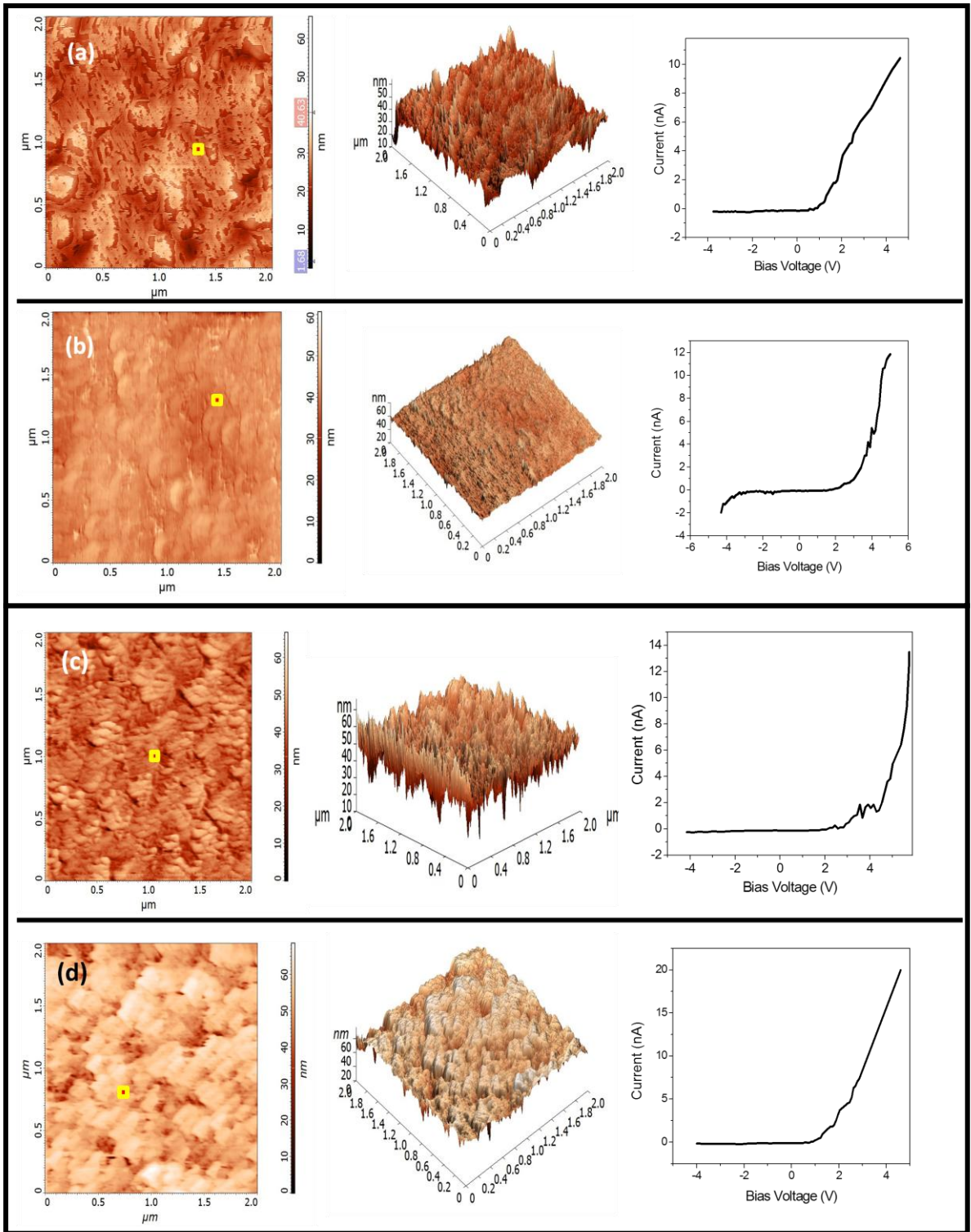


Figure 5.14: Atomic force microscopic height profile in contact mode $2 \times 2 \mu\text{m}^2$ (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt % weight of ZnO in PANi; and their corresponding 3D images and Single-point electrical I–V characteristics corresponding to the positions (squares) marked on images (a-d).

in 5 wt %, 12nA in 10 wt %, 14nA in 15 wt % and 20 nA in 20 wt % PANi-ZnO nano-composite LB films is shown in Fig. 5.15(a-d) and 5.15(e-h) their corresponding 3D images respectively. The distribution of current on the whole surface of PANi LB film is almost uniform and almost homogeneous charge transport current have been observed in the surface conductance of the PANi-ZnO LB films. This shows the film is electrically homogeneous. The distribution of current on the surface of PANi-ZnO LB films is almost uniform and very less charge transport current inhomogeneities have been observed in the surface conductance of the PANi-ZnO LB film [49]. This is also indicated from the topography of PANi-ZnO LB film in which the root mean square roughness as well as surface roughness average increases in comparison to PANi LB film [27].

5.7 Conclusions

PANi-ZnO nano-composites show good surface properties at air-water interface. Stable monolayers of organized organic-inorganic hybrid system of PANi-ZnO formed at air-water interface are efficiently transferred to solid substrate as ultrathin films by Langmuir-Blodgett technique. Electrical effects in monolayers are investigated by surface potential and dipole moment behaviour studies which reveals an increase in surface potential with increase in temperature. UV-Visible spectroscopy showed that the electronic structure of PANi is modified with inclusion of ZnO into PANi matrix. FTIR spectra show bonding between the ZnO nanoparticles and the amine groups in the PANi molecular chains. It was observed that in comparison to PANi, the IR spectra of PANi-ZnO s showed a red shift (towards lower wave-number). XRD revealed the hexagonal close-packed wurtzite structure of ZnO. The topography showed the presence of ZnO nanoparticles in the polymer chains.

Local current-voltage (I-V) spectroscopy results show that there is increase in current range in case of PANi-ZnO LB films as compared to PANi LB film. C-AFM data show almost uniform current distribution up to 10 nA in PANi-ZnO LB film. These results would make them promising films for their applications in molecular nanoelectronic devices as well as in sensors and optical devices.

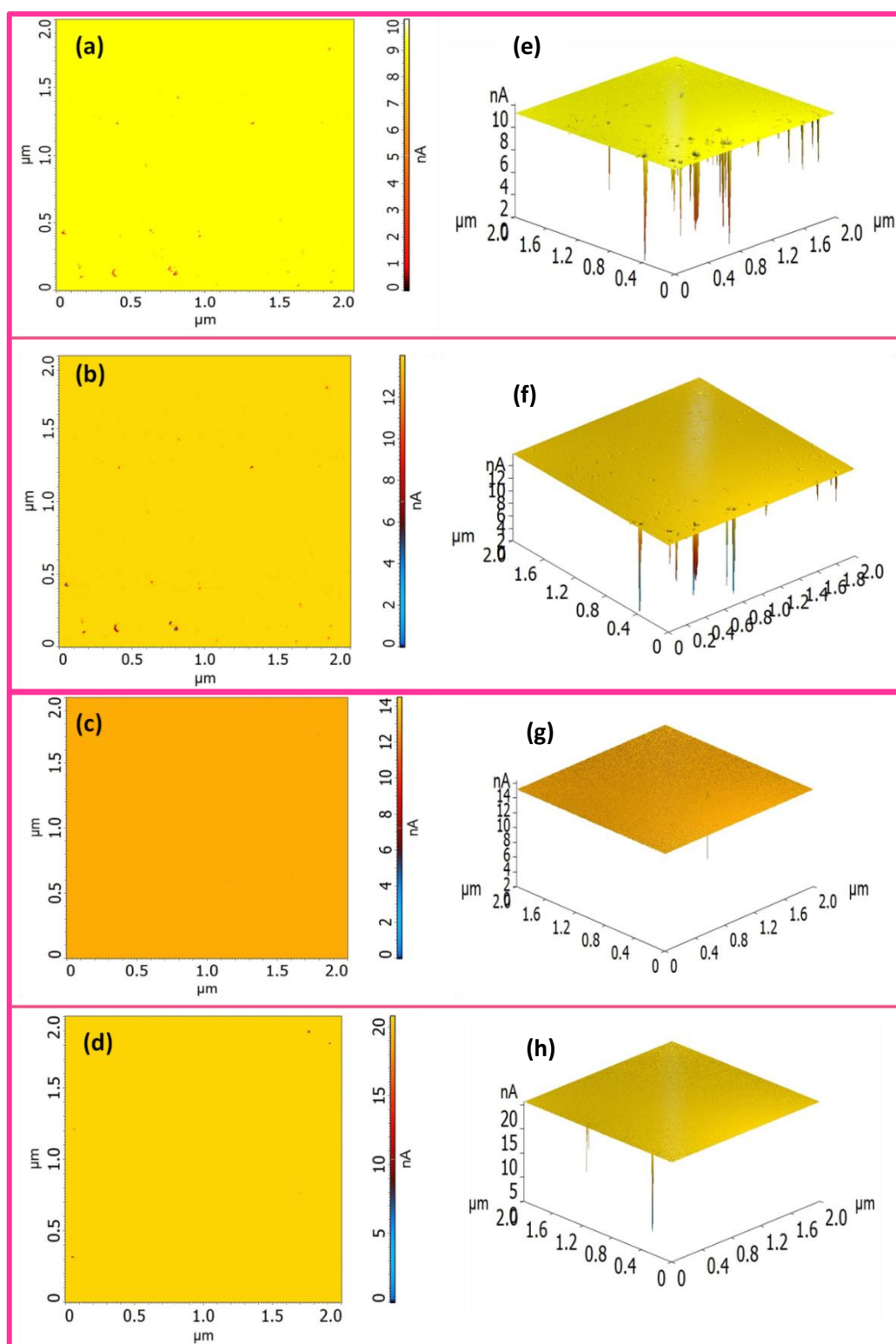


Figure 5.15: Conductive data images in Contact mode, scan range $2 \times 2 \mu\text{m}^2$ (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt % PANi-ZnO nano-composite LB films and (e-h) their corresponding 3D images, respectively.

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CHAPTER 6

CONCLUSIONS AND PROSPECT FOR FUTURE WORKS

In this thesis work the Langmuir-Blodgett technique is used to prepare organized Langmuir monolayers of conducting polymer and their nano-composite systems. Monolayers and multilayers are transferred to solid substrate by Y-type deposition (Langmuir Blodgett Technique). In this chapter, an attempt is made to understand the properties of hybrid PANi–TiO₂ and PANi–ZnO nano-composite materials at air–water and air–solid interfaces and to understand the effects of TiO₂ and ZnO nanoparticle doping on the properties of polymer thin films. The ultimate structure of these LB films could bring up possibilities of application of these composites as metallic or semiconductor components in molecular electronics. The conclusions made from studies carried out during research work of this thesis are briefly discussed as follows:

- ❖ The organization and structure of the LB films of PANi and their electrical, thermal and optical properties are characterized thoroughly. The technique of polymer-metal oxide nano-composite formation and their aggregation in thin LB films is optimized. The semi-amphiphilic nature of the PANi played a vital role in the orientation and ordering of films at interface. Electrical effects in Langmuir monolayers are investigated by surface potential and dipole moment of PANi at various temperatures is calculated. Investigations of surface potential of fluid interfaces can be a valuable tool for description, interpretation and evaluation of physical properties of monolayers as well as characterization of structure. Langmuir–Blodgett thin films of PANi were deposited on the quartz and indium tin oxide coated conducting glass substrates and investigations of their structural and optical properties by Fourier transform infrared spectroscopy, X-ray Diffraction study and UV–visible spectroscopy indicates formation of PANi LB Films. The topography of Langmuir–Blodgett films characterized by atomic force microscopy show average height profile of 25 nm. The phase imaging show composition of PANi throughout the film surface and interconnected nanofibrillar network kind morphology. Local Current-voltage (I-V) spectroscopy results by C-AFM show semiconducting behaviour of PANi LB film. Conductive data image show almost uniform current distribution through the PANi LB films. Thus LB technique provides new insight into

ultrathin films of conducting polymers, which will find a variety of applications in sensor devices. This suggests the possibility of using PANi ultrathin films in many important applications in conducting polymer based electronics and sensor devices.

- ❖ The ultrathin self assembled films of PANi–TiO₂ nano-composites were prepared and characterized successfully. FTIR study shows the presence of both TiO₂ and PANi molecules in of PANi–TiO₂ nano-composites, whereas XRD study confirmed the anatase phase and particle size of PANi–TiO₂. Electronic structure of PANi–TiO₂ and its LB film is confirmed by UV–Vis spectroscopy. Surface pressure–area isotherms indicate that TiO₂ nanoparticles are influencing the orientation of monolayer of polymer matrix. Morphology of PANi–TiO₂ nano-composite LB films shows that they are formed from nanometer-size grains of TiO₂ surrounded by interconnected nanofibers network. Local current-voltage (I-V) spectroscopy results show that there is increase in current range with increasing concentration of TiO₂ in nano-composite LB film. C–AFM data show almost uniform current distribution with increasing concentration of TiO₂ in nano-composite LB films. This work is highly useful for sensor device fabrication technology and will also find applications in other organic–inorganic electronic devices.
- ❖ PANi–ZnO nano-composites show good surface properties at air-water interface. Stable monolayers of organized organic–inorganic hybrid system of PANi–ZnO nano-composites are formed at air-water interface which are efficiently transferred to solid substrate as ultrathin films by Langmuir-Blodgett technique. Considerable shift in the isotherms towards higher area per molecule on increasing the concentration of ZnO is observed. Electrical effects in monolayers are investigated by surface potential and dipole moment behaviour studies which reveals an increase in surface potential with increase in temperature. Dipole moment study shows a rise in dipolar interaction with increase in temperature. UV-Visible spectroscopy showed that the electronic structure of PANi is modified with addition of ZnO in to PANi matrix. FTIR spectra show a slight red shift in PANi–ZnO nano-composites as compared to PANi. XRD revealed the hexagonal closed-packed wurtzite structure of ZnO. The topography showed the presence of ZnO nanoparticles in the polymer chains. The topography change significantly with root mean square roughness values between 2.8 and 4.5 nm due to the doping of ZnO. Local Current-voltage (I-V) spectroscopy results show that there is increase in current range in

case of PANi-ZnO nano-composite LB films as compared to PANi LB film. C-AFM data show almost uniform current distribution up to 10 nA in PANi-ZnO nano-composite LB film. The possibility of manipulation of the material size and shape by LB technique is of great importance for a better use of conducting properties, thus extending its applications. This work is highly useful for molecular nanoelectronic devices as well as for sensor device fabrication technology.

6.1 Future Scope of the Work

- ❖ Monolayers of polymer-nano-composite molecules were examined and deposited at pH = 6 of the subphase and at various temperatures. Monolayers can be investigated by varying pH of the subphase at different levels. As PANi exhibits both the electronic and ionic conductivity, the variation in subphase pH levels may lead to variation in conductivity due to change in oxidation state. Hence, by monitoring changes in temperature along with pH can provide new innovations in electronic technology.
- ❖ Study of dynamic visco-elastic properties (like interfacial elasticity, viscous modulus, dilational properties) of the monolayer can be obtained by using the oscillating barrier method. To measure compression isotherms using Oscillating barriers mode, Monolayer compressed to predetermined surface pressure after which the barriers start to oscillate.
- ❖ A great effort is desired in the scientific domain of fluid interfaces investigation. This is evidence that effective dipole moments can provide interesting information for thermodynamics description of the investigated system.
- ❖ Realization of electronic elements like diode based on organic-inorganic hybrid nano-composite LB films is possible as the local I-V characteristics resembles the diode characteristics. The growth of organized monolayers by the LB technique has led the research toward the goal of assembling singular molecules into highly ordered architectures.