

**Morphology controlled synthesis of polyaniline nanostructures and
its nanocomposites
using swollen liquid crystals as templates**

A Thesis

submitted

by

Sunil Dutt

(Roll No: D10008)

for the award of the degree of

Doctor of Philosophy



School of Basic Sciences

Indian Institute of Technology Mandi

Mandi, Himachal Pradesh-175005

July, 2015

Affectionately

Dedicated

To

Almighty God

&

My

loving family

Declaration

All the corrections suggested by referees have been made and provided as addendum at the end of this thesis.

I.I.T. Mandi (H.P.)
Date:

Signature of Research Scholar



Indian
Institute of
Technology
Mandi

Declaration by the Research Scholar

This is to certify that the thesis entitled “**Morphology controlled synthesis of polyaniline nanostructures and its nanocomposites using swollen liquid crystals as templates**”, submitted by me to the Indian Institute of Technology Mandi for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by me under the supervision of Dr. Prem Felix Siril. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

In keeping with the general practice of reporting scientific observation, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

I.I.T. Mandi (H.P.)
Date:

Signature of Research Scholar

Thesis Certificate

This is to certify that the thesis entitled “**Morphology controlled synthesis of polyaniline nanostructures and its nanocomposites using swollen liquid crystals as templates**”, submitted by Mr. Sunil Dutt to the Indian Institute of Technology Mandi for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by him under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

In keeping with the general practice of reporting scientific observation, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

I.I.T. Mandi (H.P.)
Date:

Research Guide

Indian
Institute of
Technology
Mandi

Acknowledgements

While pursuing my PhD degree, many seen and unseen hands pushed me forward, soul put me on the right path and enlightened me with their knowledge and experience. I shall remain grateful to all of them. I enjoyed this learning journey as a researcher.

First of all, I would like to express my deep gratitude and profound indebtedness to my PhD advisor Dr. Prem Felix Siril for his dexterous guidance, invaluable suggestions and perceptive enthusiasm which enabled me to accomplish the task of undertaking the present study. He sets an example of a world-class researcher for his passion on research. His wide knowledge and logical way of thinking have been of great value for me. His understanding, encouraging and personal guidance provided me a good basis for the present thesis.

I express my sincere thanks to The Director, IIT Mandi for his support and encouragement. The research facility at Advanced Materials Research Center (AMRC), IIT Mandi is also gratefully acknowledged hereby.

My sincere thanks to all chemistry faculty members for their invaluable advice and encouragement during course work as well as research work.

I am also very much thankful to my research group members for their invaluable support and help during my research work.

I would like to thanks to all my friends for their continuous support and encouragement.

My earnest thanks are due to AMRC staff for their assistance in lab.

A special words of thanks to my loving wife Kanchan for her continuous inspiration, motivation and cooperation.

I express profound sense of reverence to my parents for their untiring support and co-operation.

I can never forget cooperation, endless tolerance and constant encouragement from all my family members during this tough and happy moments of the journey.

Above all, all the praise is due to the Almighty God, the ultimate source of knowledge, a part of which He reveals to man and peace be upon all his Messengers throughout the world for success and guidance of mankind. I express my gratitude and indebtedness to the Almighty for countless blessings.

Table of Contents

Acknowledgements.....	i
Abbreviations.....	x
Abstract.....	xiii

Chapter 1 Intrinsically conducting polymers, polyaniline and swollen liquid crystals: An overview

1.1. Intrinsically conducting polymers and polyaniline: An overview.....	1
1.1.1. Different types of ICPs.....	2
1.1.2. Conduction mechanism of ICPs	
1.1.2.1. Band theory.....	3
1.1.2.2. Polaron and bipolaron models.....	4
1.2. Polyaniline.....	6
1.2.1. Chemical structure of polyaniline.....	7
1.2.2. Different methods for the synthesis of polyaniline	
1.2.2.1. Electrochemical method of polymerization.....	7
1.2.2.2. Chemical method of polymerization.....	8
1.2.3. Mechanism of oxidative polymerization of aniline.....	9
1.2.4. Doping of PANI.....	9
1.2.5. Different polyaniline nanostructures and its nanocomposites.....	11
1.2.5.1. General methods for the synthesis of PANI nanostructures and its nanocomposites.....	11
1.2.5.2. PANI nanoparticles (PANI-NPs)	13
1.2.5.3. One dimensional PANI nanostructures.....	14

1.2.6. PANI nanocomposites.....	16
1.2.7. Applications of polyaniline nanostructures and its nanocomposites	
1.2.7.1. Sensing applications.....	17
1.2.7.2. Energy storage applications.....	17
1.2.7.3. Microwave absorption.....	18
1.2.7.4. Environment remediation by adsorbing pollutants.....	18
1.2.7.5. Surface enhanced Raman spectroscopy (SERS).....	19
1.2.7.6. Catalytic applications.....	19
1.2.7.7. Fuel cell catalysts.....	20
1.2.7.8. Batteries.....	20
1.2.7.9. Solar cells.....	21
1.2.7.10. Electronics.....	21
1.3. Surfactants and their self-assembly.....	22
1.3.1. Lyotropic liquid crystals (LLCs) or mesophases.....	24
1.3.2. Swollen liquid crystals (SLCs).....	24
1.3.2.1. Stability of SLCs against change in chemical nature of the salts, inclusion of chemicals and materials, pH of the medium and temperature.....	26
1.3.2.2. Characterization of SLCs.....	28
1.3.3. Applications of SLCs as soft templates	
1.3.3.1. Noble metal nanostructures.....	31
1.3.3.1.1. Chemical reduction method.....	32
1.3.3.1.2. Radiolytic and photolytic reduction methods.....	33
1.3.3.1.2.1. Palladium nanostructures.....	34

1.3.3.1.2.2. Platinum nanostructures.....	35
1.3.3.2. Bimetallic nanostructures.....	36
1.3.3.3. Oxide nanostructures.....	37
1.3.3.4. Polymer nanostructures.....	37
References.....	38

Chapter 2 Synthesis of polyaniline nanostructures by confining aniline in the oil phase of swollen liquid crystals

Abstract.....	50
2.1. Introduction.....	51
2.2. Experimental section	
2.2.1. Materials.....	53
2.2.2. Synthesis of different PANI nanostructures and bulk-PANI.....	54
2.2.3. Fabrication of biosensor.....	54
2.3. Results and discussion.....	55
2.3.1. Physico-chemical characterization.....	58
2.3.2. Possible mechanism.....	64
2.4. Electrochemical sensing of hydrogen peroxide and glucose.....	67
2.5. Conclusions.....	70
References.....	71

Chapter 3 Synthesis of polyaniline nanostructures from aniline that was entrapped in the aqueous phase of swollen liquid crystals

Abstract.....	74
---------------	----

3.1. Introduction.....	74
3.2. Experimental section	
3.2.1. Materials.....	75
3.2.2. Synthesis of different PANI nanostructures.....	75
3.3. Results and discussion.....	76
3.4. Conclusions.....	80
References.....	81

Chapter 4 Gold(core)-Polyaniline(shell) composite nanowires for SERS and catalytic applications

Abstract.....	83
4.1. Introduction.....	83
4.2. Experimental section	
4.2.1. Materials.....	85
4.2.2. Preparation of the mesophases and Au _{core} -PANI _{shell} nanocomposite.....	85
4.2.3. SERS experiments.....	86
4.2.4. Dye reduction studies.....	86
4.3. Results and discussion.....	87
4.3.1. Characterization of the nanocomposite	
4.3.1.1. UV-visible absorption spectroscopy.....	88
4.3.1.2. FTIR spectroscopy.....	89
4.3.1.3. TEM imaging and EDS analysis.....	90
4.3.1.4. XPS spectroscopy.....	93

4.3.2. Mechanism of formation of the nanocomposite.....	95
4.3.3. SERS studies.....	96
4.3.4. Catalytic activity for dye reduction.....	99
4.4. Conclusions.....	102
References.....	103

Chapter 5 Controlling the morphology of polyaniline-platinum nanocomposites using swollen liquid crystal templates

Abstract.....	106
5.1. Introduction.....	107
5.2. Experimental section	
5.2.1. Materials.....	108
5.2.2. Methods of preparation	
5.2.2.1. Bulk-PANI and SLCs doped with aniline, aniline hydrochloride and hydrogen hexachloro palatinate.....	109
5.2.2.2. PANI-Pt nanocomposites.....	109
5.2.3. Instrumentation.....	110
5.3. Results and discussion.....	111
5.4. Mechanism of nanocomposite formation.....	124
5.5. Conclusions.....	128
References.....	129

Chapter 6 Facile synthesis of polyaniline-ironoxide nanocomposites using swollen liquid crystals as soft template

Abstract.....	132
6.1. Introduction.....	132
6.2. Materials and methods	
6.2.1. Materials.....	135
6.2.2. Methods.....	135
6.2.3. Dye adsorption studies.....	136
6.3. Results and discussion.....	136
6.3.1. Physico-chemical characterization.....	139
6.3.2. Mechanism of nanocomposite formation.....	145
6.3.3. Initial adsorption kinetics of cationic and anionic dyes onto PANI-Fe ₃ O ₄ nanocomposites using UV-visible absorption spectroscopy.....	147
6.4. Conclusions.....	150
References.....	150

Chapter 7 Synthesis of polyaniline-pristine graphene nanocomposites using swollen liquid crystal template

Abstract.....	154
7.1. Introduction.....	154
7.2. Experimental section	
7.2.1. Materials.....	155
7.2.2. Methods	
7.2.2.1. Preparation of exfoliated graphene.....	156

7.2.2.2. Preparations of different SLCs containing (a) aniline and graphene and (b) aniline hydrochloride and graphene and synthesis of PANI-G nanocomposites.....	156
7.3. Results and discussion	
7.3.1. UV-visible absorption spectroscopy.....	158
7.3.2. FTIR spectroscopy.....	159
7.3.3. XRD analysis.....	160
7.3.4. Raman spectroscopy.....	161
7.3.5. FESEM and TEM imaging.....	163
7.4. Conclusions.....	166
References.....	166
Chapter 8 Conclusions and future perspectives.....	170
List of Publications.....	173

Abbreviations

AA.....	Ascorbic acid
AFM.....	Atomic force microscopy
AN.....	Aniline
AN.HCl.....	Aniline hydrochloride
APS.....	Ammonium persulfate
Au-PANI.....	Gold-polyaniline
Au _{core}	Gold core
BCA.....	Butyl carbitol acetate
B-PANI or PANI-B.....	Bulk-polyaniline
CB.....	Conduction band
CMC.....	Critical micelle concentration
CNTs.....	Carbon nanotubes
CPC.....	Cetylpyridinium chloride
CPBr.....	Cetylpyridinium bromide
cryo-TEM.....	cryo-Transmission electron microscopy
CTAB.....	Cetyltrimethylammonium bromide
CTAC.....	Cetyltrimethylammonium chloride
CV.....	Cyclic voltammetry
DA.....	Dopamine
EC.....	Ethyl cellulose
EDOT.....	3,4- ethylenedioxythiophene
EDX or EDS.....	Energy dispersive X-ray spectroscopy
EF.....	Enhancement factor
EMI.....	Electromagnetic interference
FE-SEM.....	Field emission-Scanning electron microscopy
FTIR.....	Fourier transform infrared spectroscopy
G.....	Graphene

GOx.....	Glucose oxidase
HR-TEM.....	High resolution Transmission electron microscopy
ICPs.....	Intrinsically conducting polymers
IR.....	Infrared
LCs.....	Liquid crystals
LLCs.....	Lyotropic liquid crystals
MB.....	Methylene blue
MFM.....	Magnetic force microscopy
MWNTs.....	Multi walled carbon nanotubes
NFs.....	Nanofibers
NMP.....	N-methyl pyrrolidone
NPs.....	Nano particles
PANI.....	Polyaniline
PANI- Fe ₃ O ₄	Polyaniline-iron oxide
PANI-G.....	Polyaniline-graphene
PANI-NPs.....	Polyaniline nanoparticles
PANI-NS.....	Polyaniline nanostructures
PANI-Pt.....	Polyaniline-platinum
PANI _{shell}	Polyaniline shell
PANI-0D.....	Spherical polyaniline
PANI-1D.....	One dimensional polyaniline
PBS.....	Phosphate buffered saline
PEDOT.....	Poly(3,4- ethylenedioxythiophene)
POM.....	Polarizing optical microscopy
PPy.....	Polypyrrole
PtNNs.....	Platinum nanonets
PtNBs.....	Platinum nanoballs
RB.....	Rose Bengal
Rh B.....	Rhodamine B
SAED.....	Selected area electron diffraction

SAXS.....	Small-angle X-ray scattering
SDS.....	Sodium dodecyl sulfate
SERS.....	Surface enhanced Raman spectroscopy
SLCs.....	Swollen liquid crystals
SPR.....	Surface plasmon resonance
SWNTs.....	Single walled carbon nanotubes
TEM.....	Transmission electron microscopy
TGA.....	Thermogravimetric analysis
UA.....	Uric acid
UV.....	Ultra violet
VB.....	Valence band
Vis.....	Visible
XPS.....	X-ray photo electron spectroscopy
XRD.....	X-ray diffraction

Abstract

Polymers are generally known for their insulating properties. But intrinsically conducting polymers (ICPs) is the class of organic conjugated polymers that can conduct electricity. ICPs find promising applications in different fields such as in sensors, electronic devices, integrated circuits, catalysis, energy storage, memory devices etc. Polyaniline (PANI) is one of the most studied among the ICPs. PANI is more interesting due to its good environmental stability, ease of synthesis and controllable electrical conductivity through protonation/deprotonation. Properties of PANI can be tuned by nanostructuring and nanocomposite formation also and improved performance can be obtained. Exploration of novel methods for the synthesis of PANI nanostructures and the nanocomposites is thus an important research area and this is the major theme of the present thesis. Preparation of PANI nanostructures and their nanocomposites using swollen liquid crystals (SLCs) as 'soft' templates is presented in the thesis.

SLCs are a class of lyotropic liquid crystals that is usually formed from a mixture of water, oil, surfactant and co-surfactant. The aspects such as diameter of the micelles and the distance between them can be varied in SLCs and hence the name. It has been shown in the past that the SLCs can be used as versatile templates for the synthesis of a variety of noble metal nanostructures. A general method for preparing spherical and one dimensional nanostructures of PANI and its nanocomposites by using SLCs as templates has been developed and presented in the thesis. Controlling the morphology of PANI and its nanocomposites with Au, Pt, Fe₃O₄ and pristine graphene has been demonstrated using SLCs as templates in the present study. The prepared nanomaterials were thoroughly characterized using advanced characterization techniques. The PANI nanostructures and its nanocomposites were found to have interesting applications in sensing, catalysis and environmental remediation.

The present thesis entitled ‘Morphology controlled synthesis of polyaniline nanostructures and its nanocomposites using swollen liquid crystals as templates’ contains eight chapters. Chapter 1 provides an overview of ICPs, PANI, its nanostructures and nanocomposites, SLCs and their use as ‘soft’ templates. Chapter 2 describes an approach for the synthesis of PANI nanostructures by confining aniline in the oil phase of SLCs. Chapter 3 mainly focuses on the utility of the aqueous phase of SLCs for the synthesis of PANI nanostructures. Synthesis of Gold_{core}-Polyaniline_{shell} composite nanowires and their SERS and catalytic activities is described in chapter 4. Controlling the morphology of PANI-Pt nanocomposites using SLCs as templates is discussed in chapter 5. In chapter 6, synthesis of polyaniline-iron oxide nanocomposites is discussed. Chapter 7 is based on the preparation of a unique pristine graphene-PANI nanocomposite using SLCs. Chapter 8 presents the key findings of our research work and the future scope of the present work.