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

A Thesis

submitted

by


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**(Roll No: D10008)**


for the award of the degree of

**Doctor of Philosophy**


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**July, 2015**

*Affectionately*

*Dedicated*

*To*

*Almighty God*

*&*

*My*

*loving family*

Indian Institute of Technology Mandi,
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# Declaration

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

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# 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.

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# 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.

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# 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- $Fe_3O_4$…………………………………………………………..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, $Fe_3O_4$ 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.