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Abstract

A number of studies on conducting polymers relating to their synthesis, characterization, morphology and applications in various fields have been reported in literature. In spite of these interesting developments, there is a scope to improve the properties of conducting polymers and their applications.

In the present thesis, an attempt has been made in the following aspects:

(i) Synthesis and characterization of polyaniline salts, complexes, composite as well as novel optically active polyaniline by aqueous and emulsion polymerization pathway, and evaluation of polyaniline as recyclable polymer based solid catalysts for various organic transformations.

(ii) Evaluation of polyaniline-maleicacid-dodecylhydrogensulfate salt-coated ceramic material as gas sensor material for various toxic gases such as NH_3, CO_2, SO_2 & H_2S.

(iii) Preparation, characterization of polyaniline 3D nanofiber networks using sulfonated-*p*-cresol as novel dopant by inverted emulsion polymerization method and evaluation as gas sensor material for ammonia gas sensor.

(iv) Preparation, characterization of nanostructured (dendrite) polyaniline-polystyrene film and evaluation as ammonia sensor.

(v) Synthesis and characterization of nanoporous polyaniline salt using ternary surfactant as novel soft template.

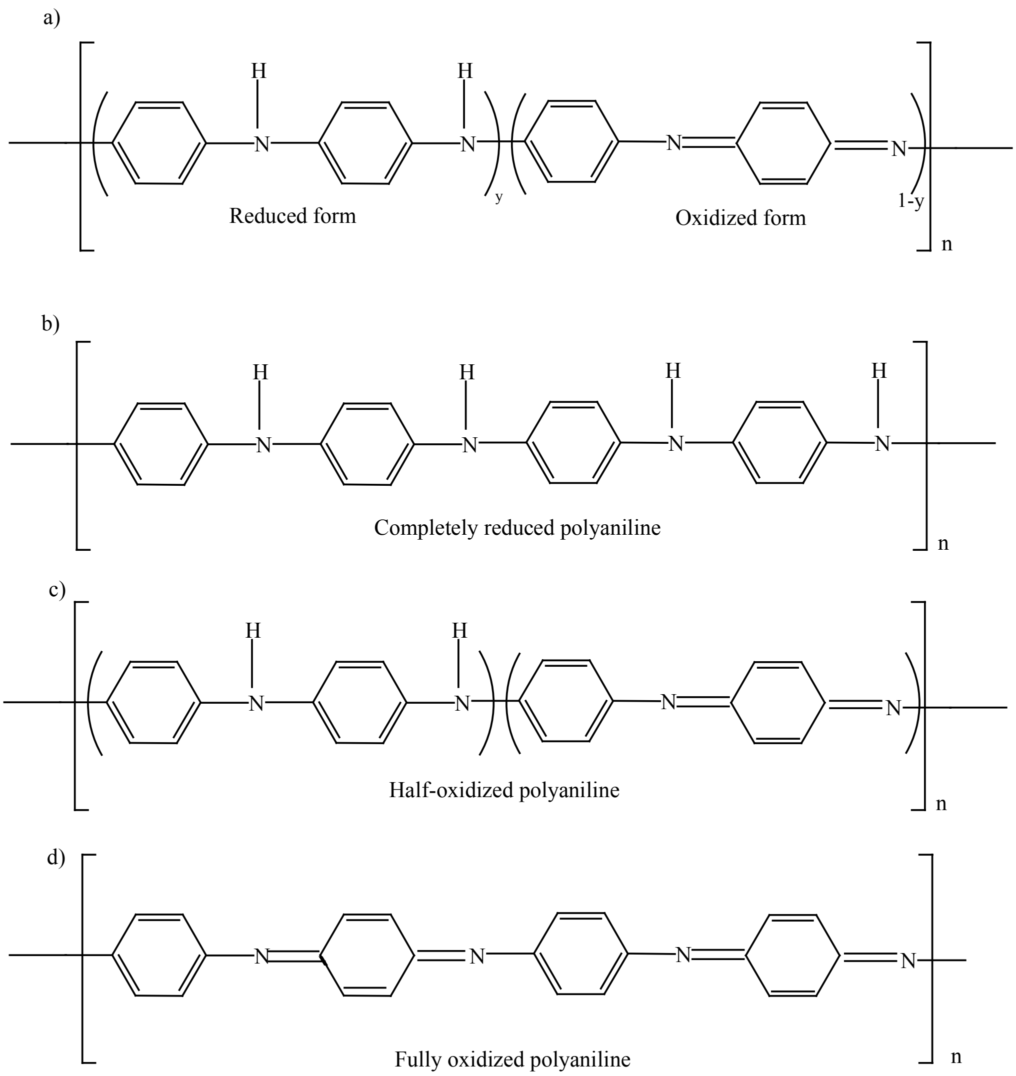
This thesis is divided into five chapters.

Chapter 1: Introduction

In this chapter a review of intrinsically conducting polymers (ICPs) with emphasis on conducting polymers is presented. Conducting polymers have emerged as an important class of electronic materials because of their potential applications as catalyst, electrochromic displays and microelectronic devices etc. A large number of conducting polymers such as polyacetylene, polypyrrole, polythiophene and polyaniline have been synthesized and characterized in recent years. Among these conducting polymers, polyaniline has been considered as an extremely interesting and unusual member of polymers having the delocalized π electrons. Conducting polyaniline is basically poly (paraphenylene amineimine) in which its oxidation state can be varied from the fully oxidized (pernigraniline) to fully reduced (leucoemeraldine) states. The most stable emeraldine state is 50% oxidized form of polyaniline (Figure 1).

A number of studies on conducting polyaniline relating to their structure, morphology, electrochromic and solid-state properties have been reported in literature. The literature provides an account of various routes adopted in the synthesis of conducting polyaniline for its potential applications. Extensive research is being carried out on conducting polyaniline throughout the world. However, synthesis of commercially valuable conducting polyaniline material is still a challenging research. In this regard, we have synthesized and characterized various conducting polyaniline materials by simple routes. Organic transformations were carried out using polyaniline salts, complexes, composite and optically active polyaniline as reusable polymer based catalyst. Sensor studies for various toxic gases (NH_3, CO_2, SO_2 & H_2S) were carried out using polyaniline materials in the form of bead, pellet and film.

Figure 1: Different states of polyaniline.



Chapter 2: Characterization techniques and materials

The various techniques adopted to characterize the polyaniline salts, complexes, composite, film, optically active polyaniline base and organic compounds are briefly discussed in this chapter. The preparation of samples for analysis and materials for synthesis are also described.

Chapter 3: Organic transformations by polyaniline catalysts

This work deals with the synthesis of polyaniline salts, complexes, composite as well as novel optically active polyaniline by aqueous and emulsion polymerization pathway, their characterization and evaluation of polyaniline as recyclable polymer based solid catalysts for various organic transformations.

3A: Polyaniline salts, complexes and composite as polymer based solid acid catalyst

In this work, polyaniline salts, complexes and composite were investigated as polymer based solid acid catalysts for various organic transformations such as protection (Yields: 85-98%) and deprotection of aldehydes (90-96%), synthesis of bisindoles (38-99%) and condensation reaction for the synthesis of coumarins (92%).

3B: Chiral polyaniline base catalyst

An optically active polyaniline [Poly(2-anilinomethylpyrrolidine)] was synthesized, characterized by circular dichroism, UV-Vis, FT-IR as well as NMR analysis and used as an organo polymeric base catalyst for Aldol reaction (20-73%).

The effect of the nature of the catalyst, amount of catalyst, mole ratio of reactants, time, solvents and temperature of reaction were studied to establish the optimum reaction conditions. The reusability of the polyaniline based solid acid & base catalysts were checked by employing the recovered catalyst in the reactions. The synthesized polyaniline based catalysts were successfully evaluated as solid acid or base catalyst with desired features such as easy preparation, easy recovery, simple work-up procedure, higher yield, less time, reusable and eco-friendly nature.

Chapter 4: Polyaniline as sensor materials for toxic gases

4A: Sensing properties of polyaniline-maleicacid-dodecylhydrogensulfate salt to the toxic gases

This chapter deals with the results of novel polyaniline-maleicacid-dodecylhydrogensulfate salt coated ceramic material as gas sensor, capable of operating at room temperature for toxic gases (Chapter-4A). The change in resistance of polyaniline materials for NH_3, CO_2, SO_2 & H_2S gases at different concentrations (10, 100, 1000 & 10000 ppm level) was monitored for sensor characteristics. The stability of the polyaniline material under continuous exposure of different gases was also studied. This novel gas sensor material has desirable features such as excellent sensing ability, stability, low cost, fast regeneration time (~1-2 min), operable at room temperature with simple experimental set up.

4B: Polyaniline-3D nanofiber network synthesized by inverted emulsion polymerization route: Sensor material for ammonia gas

This work deals with the synthesis and characterization of polyaniline-3D nanofiber network *via* inverted emulsion polymerization pathway using sulfonated-*p*-cresol (SPC) as novel dopant, benzoyl peroxide (BPO) as oxidant and sodium lauryl sulfate (SLS) as surfactant (Chapter-4B). The synthesized polyaniline salt in 3D nanofiber networks having an average diameter 40-160 nm and reasonable conductivity (0.1 S/cm), were obtained in high yields (134 %) with the use of [SPC]/[An] ratio 3, [SLS]/[SPC] ratio 0.1 and benzoyl peroxide [BPO] (0.12 M) under stirring condition at a temperature of 40°C for 24 hrs. This polyaniline in 3D nanofiber salt was well characterized by SEM, infrared, electronic absorption spectroscopy, X-ray diffraction and elemental analysis.

The synthesized polyaniline nanofibers has been evaluated as sensor material for ammonia gas with advantages such as less response time, fast reproducibility, operable at room temperature with simple experimental set up.

4C: Synthesis of polyaniline-polystyrene (PPSt) film by solution blending technique: Sensing properties for ammonia gas

In this work, PPSt films were prepared by solution blending with increasing amount of polyaniline, i.e. 3.7 (1 mL), 7.2 (2 mL) and 10.4 (3 mL) wt%. PPSt film was well characterized by resistance measurements, SEM, infrared spectroscopy, TGA and UTM techniques (Chapter-4C). Scanning electron microscopy (SEM) of the PPSt film prepared using 10.4 wt% polyaniline solution showed a nanostructured (dendrite) morphology. The prepared nanostructured film was tested for its efficacy as sensors to ammonia gas by monitoring the changes in resistance. The PPSt film had several advantages such as high reproducibility, low response time and ability to be operate at room temperature with simple experimental set up.

4D: Synthesis of nanoporous conducting polyaniline using ternary surfactant

This work deals with the preparation of novel nanoporous polyaniline using ternary surfactant [a mixture of CTAB (cationic), SLS (anionic) and F-68 (nonionic surfactants)] as a soft template by aqueous polymerization method (Chapter-4D). The influence of synthesis conditions such as time of polymerization, temperature of the reaction, acids, oxidizing agents and reaction condition (stirring/static condition) etc., on the properties of porous polyaniline (PANI) were investigated. The synthesized PANI was well characterized by SEM, TEM, FT-IR and X-ray diffraction analysis. Nanoporous PANI in good yield (84 wt % with respect to aniline used) and reasonable conductivity (10^{-2} S/cm) with 100 nm range was obtained under the following reaction conditions: sodium persulfate-1.19g, R-CSA-2.32g, constant stirring for 4 hrs at 0-5°C. Sensor studies on the porous PANI material revealed that this material does not show sensitivity to toxic gases.

Finally, as an extension of our research work, we have synthesized and characterized the following materials:

- A stable polypyrrole salt by inverted emulsion polymerization pathway using benzoyl peroxide as novel oxidizing agent, *p*-toluene sulfonic acid as dopant and sodium lauryl sulfate as surfactant.
- Nano and microspheres of novel poly(aniline-formaldehyde) under static condition by a simple mixing process using a mixture of metal chlorides ($FeCl_3$+$AlCl_3$).

Chapter 5: Summary

The results of the thesis work are summarized in this chapter.