

A Review on Analysis and Testing of Conducting Polymer and Nanocomposites on the basis of their Conducting Properties

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ABSTRACT

The main motive behind this research is to eradicate the limitations of the conducting polymers and replace these materials with newly emerging materials known as 'Nano-composites' because of their superior electrical and mechanical properties. The various naturally occurring inorganic nanoparticles which are when combined with conducting polymers leads to the generation of a host of nanocomposites which has very fascinating properties as well as adequate application potential. In this paper, various fundamental materials along with their conducting properties that are employed for synthesis of nanocomposites such as nano materials and conducting polymers have been analyzed and discussed. The Graphene-based polyaniline (PANI) nanocomposites have been used in the proposed formation of hybrid material comprising of conducting polymer and carbon nano material. The Polyaniline/Graphene nanocomposites (PANI/G) are synthesized on the basis of graphene to polyaniline (PANI) ratio. The PANI is known for its low cost, good environmental stability, interesting electro activity, high pseudo capacitance which makes this material to be suitably employed for electronic, optical and electrochemical applications. Polyaniline/Graphene nanocomposites (PANI/G) are synthesized at various loadings of graphene to polyaniline (PANI) ratio.

Keyword: Polyaniline (PANI), Graphene, Carbon nanotube (CNT) Nanocomposites.

INTRODUCTION

Over the past decade, there has been significant progress in fabricating nanostructured materials with unique properties. CPs are polymeric materials that display high conductivities, good electrochemical activity, unique optical properties, CPs have reached special attention as promising candidates in many areas of nanoscience and nanotechnology. CPs also known as conjugated polymers or "synthetic metals" are polymers with highly pie conjugated polymeric chains. A variety of CPs (eg. Polyaniline (PANI), Polypyrrole (PPy), polythiophene (PT), poly(3,4-ethylenedioxythiophene) and other PT derivatives) have been developed. Hybrid nanomaterials, the combination of CPs with different types of materials, such as metals, carbonaceous



materials, inorganic compounds, have been studied most intensively. Such nanohybrids have proven to be attractive for a wide variety of applications, from organic electronics to energy storage, solar cells, and sensors.[1]

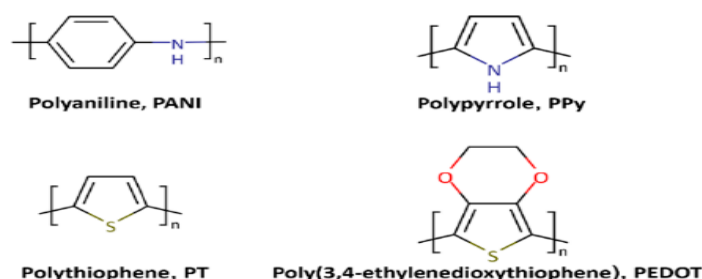


Figure 1: Chemical structures of representative conducting polymers (CPs).

Conductive polymer, such as Polypyrrole (PPY) and Polyaniline (PANI), have shown a special capability to rapidly and reversibly switch between distinct oxidation states[2,3] which plays a vital role in biocommunication. Moreover, the various biomolecules can be incorporated into conducting polymer by electrochemical polymerization. These two abilities make conducting polymers suitable enough for application in the area of bio sensors[4,5]. The synthesis of conducting polymer films has thus recently been a significant subject of intensive research. PPY is the most thoroughly examined one among various conducting polymers for biological applications because of its high electrical conductivity in a wide range of pH values, flexible method of preparation, ease of surface modification, excellent environmental stability, ion exchange capacity and biocompatibility[4,6,7,8,9,10]. But one of the properties that hinder the development of electrochemically synthesized PPY film is its flat surface with restricted surface area. This has been reduced to some extent by template methods. Method of polymerizing pyrrole within porous materials was employed to improve the surface area of PPY[9,10]. Arrays of PPY dots (80-180 nm diameter) were generated by using diblock copolymer surface micelle arrays as reaction template[11]. The method of preparing multilayer polymer composite film on the base of PANI[12], Polythiophene[PMET-PPY], polysiloxane [13] etc. was also used to improve the surface area of PPY and the continuous films with microscaled structure was collected.[14]

Synthesising of conducting polymer

The synthesis of Polyaniline samples was attained using a chemical method by oxidizing the corresponding monomer. Aniline in the presence of an oxidizing agent Ammonium persulphate (APS). The solution of aniline with DI water changes colour from transparent to green to brown to dark blue which is an indication of the oxidizing reaction taking place. In order to further enhance the surface to volume ratio of the synthesized Polyaniline, camphor Sulphonic acid (CSA) is used to enable the material to form nanostructures. The reaction has to be carried out at zero degree Celsius and hence the entire experimental setup is placed on an ice bath. The experiment is performed in a laminar air flow bench which prevents contamination by dust and other small particles. All the solutions are kept in an ice bath. A Magnetic bead is added to the beaker containing the aniline solution and the beaker along with the ice bath is placed on a magnetic stirrer set to about 800 rpm. The CSA solution prepared is transferred into a burette and added dropwise into the aniline solution. This enables the formation of nanostructures. The APS solution is then transformed into a burette and then added dropwise into the beaker and continuously stir it. The oxidization of the monomer occurs immediately and the colourless solutions starts changing colour to green, then to dark shades of brown and finally dark blue or violet. The Polyaniline precipitate formed is filtered using a funnel lined with Whatman filter paper. After leaving it for an appropriate amount of time, a precipitate is collected on the filter paper. Polyaniline formed on the filter paper is dried in vacuum at 60 degrees and a powder form of aniline is obtained. This process is repeated by varying the composition of the various components involved to obtain several samples. Polyaniline, being an organic material, leads to disintegrate at high temperatures. Thus, to obtain thin film coatings of polyaniline, the spin coating technique is selected for its ability to produce uniform films without requiring high temperatures such as in CVD and sputtering.

Characterization

The Polyaniline based sensors were characterized using various techniques for analyzing chemical and electrical properties.

FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An infrared spectrum signifies a fingerprint of a sample with absorption peaks which corresponds to the frequencies of vibrations between the bonds of the atoms forming the

material. Therefore, FTIR spectroscopy can produce positive identification (qualitative analysis) of a different kind of material.[15]

UV – V analysis

This can be employed for the quantitative analysis of the Ultraviolet – visible spectroscopy explains the absorption spectroscopy or reflectance spectroscopy in the ultraviolet visible spectral region. The absorption or reflectance in the visible range directly affects the perceived colour of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. The absorption spectrum measures transitions from the ground state to excited state. Organic compounds, specially with a high degree of conjugation absorb light in the uv or visible regions of the electromagnetic sample.

Testing Circuit for sensor

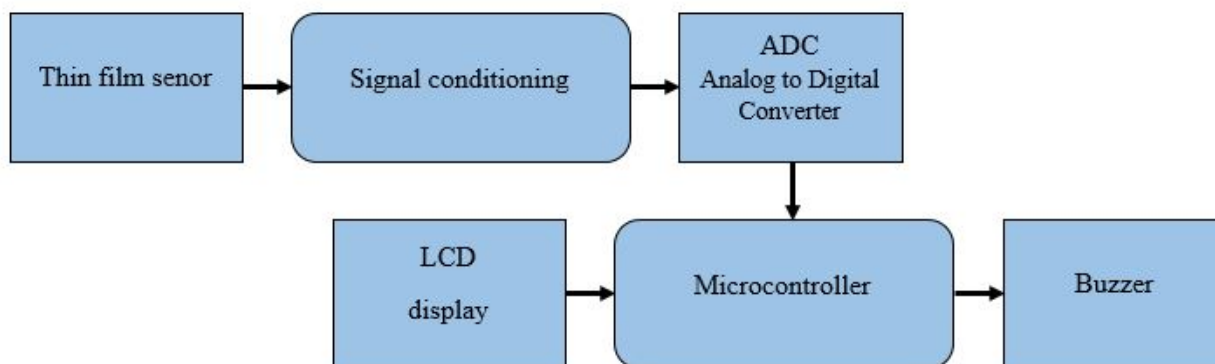
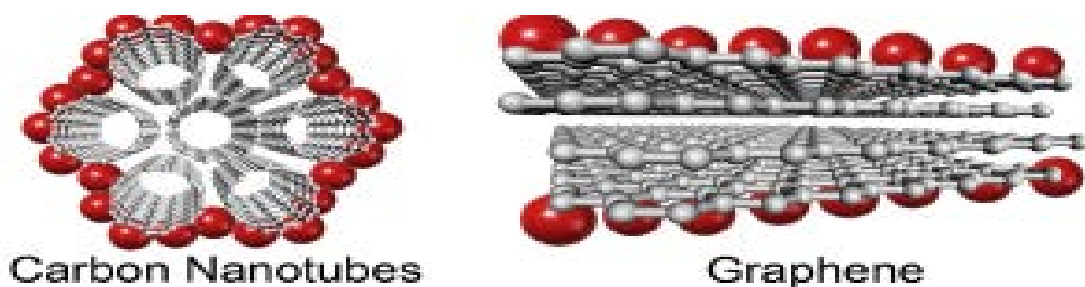


Figure 2: Block diagram for testing circuit for sensor

The sensor is interfaced to a data acquisition system comprising of a signal conditioning circuit and an ADC interfaced to a microcontroller to process the data. The system produces the visual warning using the LCD and an audio warning utilizing buzzer. The conducting polymer based thin film gas sensor causes a change in conductivity and thus its resistance when subjected to the presence of the target gas. This change causes the resistance of sensor to be measured as a change in voltage. This is accomplished using the signal conditioning circuit.[16]

Carbon nanomaterials

High energy density has been obtained by using graphene and single – walled carbon nanotube(CNT) composite electrodes in symmetric supercapacitors[17].The low electrical conductivity of activated carbon is also limiting its applications in high power density supercapacitors and results in a low specific capacitance per area. Carbon nanotubes, specially single walled carbon nanotubes(CNTs) have improved electrical conductivity and large surface area. Graphene and chemically modified graphene sheets possess a high electrical conductivity, large specific surface area and good mechanical in comparison to CNTs.The specific surface area of a single graphene is much larger than that of activated carbon and carbon nanotubes that are usually used in the electrochemical double- layer capacitors[18,19,20,21,22,23]. Graphene nanosheets tend to form irreversible agglomerates or even re- stack to form graphite through VanderWaals interactions during the process of drying.Graphene usually has an electrically conductivity of about $100 - 200 \text{ S m}^{-1}$, which is two orders of magnitude lower than conductive CNTs.



The PANI coated graphene/CNT composite electrodes are employed without any binder in order to reduce the interfacial resistance and to increase the electrochemical reaction rate.

Preparation of Graphene /CNT – PANI composite

The preparation is done in the following steps

1. Graphene oxide

Graphene oxide was synthesized by using a modified Hummers- Offeman method from graphite [22].Graphiite and NaNO_3 were first mixed together in a flask before H_2SO_4 (95%)

was added to the flask. Potassium permanganate was then added to the suspension. The colour of the suspension would become bright brown after stirring. The mixture was finally washed by rinsing with 5% HCL and then demonished water . After centrifugation , filtration, and drying in a vaccum, graphene oxide was collected in the form of powders.

2. Reduction of graphene oxide

Graphene oxide was first dispersed in distilled water sonicated. The suspension was then heated and hydrazine hydrate was added into the suspension. The reduced graphine was obtained by filtration in the form of black powders. The obtained material was finally washed using distilled water again to eradicate the excessive hydrazine.

3. Preparation of graphene/CNT – PANI composite

To make the graphene/ CNT – PANI Composite, graphene and CNTs were first dispersed and mixed in ethanolto obtain a uniform graphene/ CNT composite film by vaccum filtration using a PTFE filter paper of 250 nm in porosity. Electrodeposition of PANI was conducted using a three – electrode system and a platinum sheet was used as the counter electrode. Anodic deposition was controlled by a potentiostat in HCL electrolyte containing the aniline monomer[23].The PANI nano- cones were synthesized in two steps- nucleation of the PANI, obtained at constant potentialand growth of the PANI nano- cones obtained at constant current.[24]

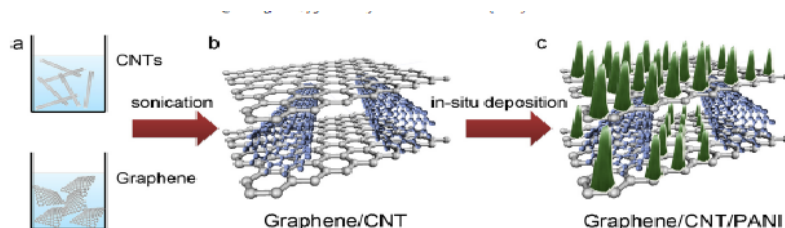


Figure 3. Illustration of fabrication of graphene/CNT – PANI composites (a) Graphene and CNT suspensions are mixed together by sonication and then made into graphene / CNT composite by vacuum filtration(c)Graphene / CNT paper is coated with vertically aligned nano-cones by anodic in situ deposition to make graphene / CNT – PANI composite.

Conclusion:

The motive behind this research is to characterize and synthesize various nanocomposites or nanostructures and their performance is analyzed using various techniques such as FTIR analysis, UV analysis, etc. Moreover, these nanocomposites are tested on the basis of signal

conditioning and results are experimentally verified in terms of audio and video signal using Buzzer and LCD display respectively. It has been concluded from the above research that nanocomposites are much better than conducting polymers for the synthesis of Nanosensors because of their good conducting properties in comparison to conducting polymers.

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