# CHARACTERIZATION OF COBALT DOPED NANO STRUCTURED POLYANILINE CONJUGATE POLYMER.

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## ABSTRACT

Due to their outstanding properties, conducting polymers have been extensively studied because of their outstanding properties, including tunable electrical property and optical and mechanical properties, easy synthesis and fabrication, and high environmental stability over conventional inorganic materials. When combined with other materials, conducting polymers transcend many of the inherent limits of their pure state. These polymer nanocomposites are promising functional nanomaterials for a variety of applications because of their easy processing. Photocatalytic oxidation technique is one of their most promising areas of use. Using Co-doped ZnO nanorods as a starting point, polyaniline (PANI) nanocomposites may now be made. It was proven by XRD and UV–visible absorption measurements that wurtzite ZnO nanostructures with Zn sites substituted by Co ions in the ZnO host structure were formed by hydrothermal method with molar ratio between cobalt and zinc precursor salts reaching 0.07. The contact between produced nanorods and the PANI matrix was established by HR-TEM morphological analysis of PANI/Co-doped ZnO nanocomposites.

**KEYWORDS** Nano Structure polyaniline, conducting polymers, PANI, X-ray diffraction (XRD),

## INTRODUCTION

There has been a growing need for renewable sources of power because of rising energy needs and the depletion of fossil fuels. It is equally important for the growth of industry and human well-being to store energy. Electric energy storage systems that are high-energy density, low-cost, environmentally-friendly, and long-lasting are needed to address the difficulties of portable and flexible cutting-edge electronics' energy storage needs in the next years (ESS). Customers now have the option of using batteries or super capacitors (SCPs) to power their portable gadgets. Lithium-ion batteries (LIB) and lead-acid batteries (LA) have reached full commercial maturity. Each of these batteries has its own set of advantages and disadvantages. Specifically, the lead-acid batteries lower volumetric energy density and usage of lead as an electrode material make it unsuitable as a long-term energy storage option for future sustainable energy management. Optoelectronics has undergone a major revolution because to the development of electroactive polymers, which are polymers with exceptional optical and electrical capabilities. Environmental stability, synthesis simplicity, optical and electrical characteristics that may be tailored — these are just some of the benefits that come with these conjugated polymers. Some changes in the polymer's oxidation and protonation states may affect its characteristics.

## LITERATURE REVIEW

**JOAQUÍN RAFAEL CRESPO-ROSA ET.AL (2021)** AuNPs embedded in conducting polymers (nCPs) derived from aniline, thiophene and 3,4-ethylenedioxythiophene were synthesised using a one-pot sonochemical approach in this investigation. It took just 5–10 minutes to synthesise the nanocomposite (nCPs-AuNPs) using high-energy ultrasound and a CP precursor monomer and KAuCl4 in the presence of LiClO4 as a dopant in an aqueous solution. There are a number of advantages to this method over other methods that have previously been described. For the first time, it was possible to produce large amounts of doped polyaniline PANI-AuNPs nanofibers. As a result, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), and Fourier transform infrared spectroscopy (FTIR) were all used to examine them (EIS). The enzyme glucose oxidase was immobilised using PANIAuNPs nanofibers as an immobilisation matrix (GOX). Finally, the so-obtained GOX-PANI-

AuNPs/Sonogel-Carbon biosensor was used to measure glucose in genuine samples of white and red wines, yielding remarkable recoveries (99.54 percent ). As a result of our study, we want to gain new insights into the production of nanostructured conducting polymers and encourage further investigation of these nanocomposites, particularly in research domains such as (bio)sensors and catalysis.

**Susmita Dey Sadhu et.al (2020)** X-ray diffraction (XRD), thermo gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and transmission electron microscopy (TEM) measurements characterise these doped polyaniline (PANI), polythiophene (PTH), and their copolymers (by interfacial and aqueous polymerization) with monomers at 50:50 ratios. An interfacial polymerization copolymer is combined with a chemically produced copper oxide nanoparticle at a loading concentration of 0.2 percent. PANI and polythiophene were shown to have amorphous structures by XRD analysis. Copper oxide nanoparticles have a distinct peak at 2 = 36.45, but the copolymer (interfacial polymerization) and the copolymer Nanocomposites have several peaks, both of which indicate crystalline structure In terms of TGA measurements, the interfacial polymerization copolymer is stable between PANI and polythiophene. Aniline and thiophene units are found in the interfacial copolymer, according to FTIR spectroscopy. A copolymer is formed when two or more monomers are chemically bonded together (by interfacial and aqueous polymerization). The appearance of a peak at around 1103 cm1 verifies the creation of NS bonding in the interfacial copolymer by interaction between aniline and thiophene. TEM pictures have demonstrated the nanoparticles' homogeneous dispersion inside the copolymer matrix (a polymer formed by interfacial polymerization). Copolymers and copper oxide have different electrical characteristics than polymers. Nanocomposite materials are investigated, and it is discovered that the copolymers increase conductivity more effectively than the individual polymers do. Interfacial copolymer conductivity is increased by 15.24-fold with a copper oxide nanoparticle loading of 0.2 percent.

**HEE JAE HONG ET.AL (2019)** Polymer flexibility can now be quantified. Instead of being the opposite of brittleness, the two equations are compared to see how flexible Y is. For example, the term "flexibility" covers the volume of a substance, as well as the total of the strength of chemical bonds. When plotting the flexibility as a function of friction, a single curve is created for polymers.

**KINGSLEY KEMA AJEKWENE ET.AL (2018)** This research describes the chemical oxidative polymerization at room temperature of conducting polyaniline (PANI) using aqueous hydrochloric acid (HCl) as a doping agent and ammonium persulfate (APS) as an oxidising agent. For both bulk and nanoscale particle sizes, several formulas have been applied. The morphology of the PANI was studied using scanning electron microscopy (SEM). FTIR spectroscopy, XRD spectroscopy, and UV-Vis spectroscopy were utilised to analyse the produced PANI. Measurement of the thermal behaviour of the samples was done using thermo gravimetric (TGA) and differential scanning calorimetry (DSC). Due to the change in polymerization method, FTIR analysis indicated the development of PANI and a structural change in the polymer structure. SEM confirmed this. In the absence of breakdown, the weight loss patterns of bulk PANI-HCl and nano-structured PANI-HCl were found to be identical, but the weight loss of nano-structured PANI-HCl was somewhat lower. While bulk PANI-HCl had a conductivity of 0.127 S/cm-1 at ambient temperature, the conductivity of nano-structured PANI-HCl was measured at 0.478 S/cm-1.

**SUNANDANA MANDAL ET.AL (2017)** A polyaniline, polyaniline nanoparticles, and polyaniline composite composite synthesis is described here. Composites and nanocomposites of aniline may be formed, or mixes with commercially available polymers or inorganic materials that give improved mechanical and optical qualities, stability, and processing capabilities can be made. Because of this, conducting polyaniline nanostructures (nanoparticle, nanorod, nanowire) are a hot topic of study. These nanoparticles were synthesised using sonochemical procedures. The TEM pictures of the nanoparticles were used to identify them. Analine monomer was chemically oxidised in the presence of polyethylene glycol and Ag nanoparticles to form aniline-based PANI/PVA nanocomposites. A paper disc diffusion technique was used to test the antibacterial activity of the synthesised nanocomposite against Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli), both of which are Gram positive bacteria. The antibacterial analysis revealed that the PANI/PVA composite had poor antibacterial activity, however PANI/PVA/Ag composites were effective against two microorganisms.

## EXPRIMENTRAL

Oxidative polymerization was used to produce polyaniline. Chemical grade cobalt (II) salts, such as acetate and chloride, were available. The synthesis of Co (II) salen has been carried out as stated. There were no issues with immobilising the salts and complexes on PANI. Cobalt(II)-based catalysts were synthesised using the following steps.

## POLYANILINE SUPPORTED CATALYSTS SYNTHESIS: METHOD I.

The polyaniline (500 mg) and cobalt acetate (500 mg) were mixed for 72 hours at room temperature in a 25 mL MeCN/HOAc mixture. It was then filtered and the solid catalyst was washed with MeCN (5 mL) in order to remove any remaining impurities. It was dried for 24 hours at 110°C.

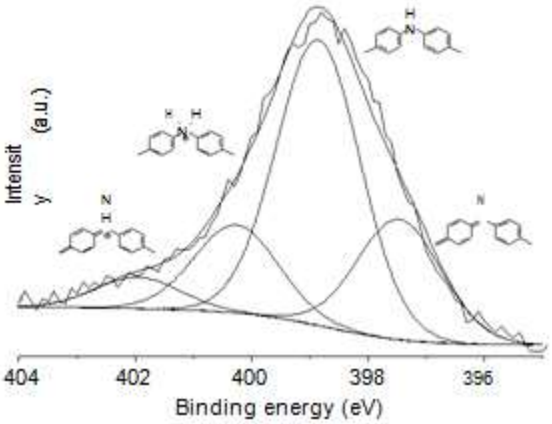


**Figure 1: Representative N1s spectra of polyaniline cobalt (II) supported catalyst.**

Chemical bonding on the surface can be determined more accurately with careful examination of the XPS spectrum. Several studies have shown that the N1s spectra of polyaniline may be represented by four separate polyaniline units at eV 398.20, 399.40, 400.7, and 402.6, each of which can be attributed to a different N1s component (Figure 1).

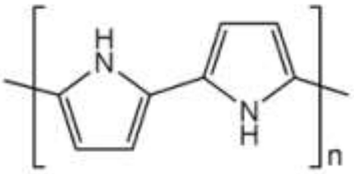
## METAL-INSULATOR TRANSITION IN DOPED CONDUCTING POLYMERS

Conducting polymers' metal-insulator transition (M-I) is one of the most intriguing physical characteristics of the materials. Coherent metallic transport is impossible when the mean free path is less than the inter-atomic separation in a metallic system. Eventually, if the disorder is great enough, the metal will stop acting like metal and start acting like an insulator. A Fermi glass with a constant density of locally occupied states, according to Fermi statistics, is formed when this transition, also known as the Anderson transition, causes all of a conductor's states to become localised. Even though there is no energy gap in a Fermi glass, it functions as an insulator because of the spatially confined energy levels. An Anderson transition-critical material exhibits power law temperature dependency in terms of electrical conductivity. Different conducting polymers including Polyaniline, Polypyrrole, Poly(p-phenylene vinylene) and Polyacetyle have all shown this M-I transition, which is especially fascinating since it occurs across a broad temperature range. Tweaking the degree of disorder by doping or adding external pressure and/or magnetic fields may readily change the critical regime in conducting polymers.

As T decreases to zero in the metallic domain, the zero-temperature physical phenomena stays finite and (T) is constant. Although disorder is widely acknowledged to have a significant role in the physics of metallic polymers, the effective length scale of the disorder and also the type of the M-I transition are crucial considerations.

These conducting chemical compound composites include Polyaniline (PANI) and Polypyrrole (PPy), two of the most popular host conducting polymers.

Chemical changes to Pyrrole (PPy) may provide a new organic chemical molecule known as Polypyrrole (PPy). conducting polymers are a common term for this kind of material. Polypyrrole and others were recognised in 2000 for their contributions to the field of conductive polymers with the Nobel Prize in Chemistry.



This is the most typical method for making PPy, and it involves utilising ferric chloride in methanol:

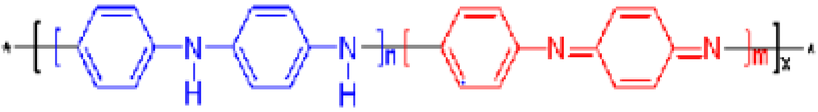
$$n\ C_4H_4NH + 2\ FeCl_3 \rightarrow (C_4H_2NH)n + 2\ FeCl_2 + 2\ HCl$$

The pi-radical cation C4H4NH+ is hypothesised to be formed during polymerization. The C-2 carbon of an unoxidized pyrrole molecule is attacked by this electrophile, resulting in a dimeric cation (C4H4NH)2 ++. The procedure is repeated numerously. In order to create conductors, PPy must be oxidised (p-doped).

$$(C_4H_2NH)n + x\ FeCl_3 \rightarrow (C_4H_2NH)_n\ Cl_x + x\ FeCl_2$$

The electrochemical process may also effect polymerization and p-doping. After that, semiconductive polymers form on the anode's surface. It has been hypothesised that metal electro-catalysts (Pt, Co, etc.) once coordinated with the atomic number 7 within the Pyrrole monomers show increased chemical element reduction activity, so Polypyrrole is also being investigated in temperature cell technology to extend catalyst dispersion within carbon support layers and sensitise cathode electro-catalysts (see above).

Polyaniline is found in one of three chemical reaction states where the inexpensive phenylamine molecule has been polymerized.



## Polyaniline (PANI)

The degree of chemical activity is shown in the image above as x = 0.5. (DP). The reduced state of leucoemeraldine is n=1, m=0. Rather of alkane series linkages, pernigraniline has imine links instead of being completely oxidised (n=0, m=1). It's been discovered that the majority of Polyaniline forms are in one of the three states or physical combinations of these sections. If the acid protonates the imine nitrogen, the emeraldine (n=m=0.5) polyaniline is known as emeraldine salt (ES), and it is neutral if doped (protonated). Diiminobenzene and diiminoquinone are able to delocalize through protonation, a process that would otherwise be impossible. Because of its great temperature stability and the fact that the resulting emeraldine salt form of Polyaniline, when doped with acid, is exceptionally electrically conductive, emeraldine base is regarded the most useful variety of Polyaniline. Even when doped with acid, leucoemeraldine and permigraniline are weak conductors.

The electrical conductivity of emerald is ten times higher after it has been treated with acids. To produce conductivities of 4.60x10-5 S/m, four percent HBr must be included into Polyaniline's structure. Leucoemeraldine reaction will produce a comparable substance. For its widespread usage in computer circuit board manufacturing and corrosion prevention, polyaniline relies on the fact that it is nobler than copper and somewhat less noble than silver.

## CONCLUSION

Electronics and electrical domains benefit from the use of nanocomposite particles. The Silica-Polyaniline composites are used to analyse the study on Oxalic acid. The particles are less than 2.00um in diameter, according to SEM examination. It has been shown that the composite structures include silicon oxygen, oxalic acid, and polyaniline connections. UV spectra are used to validate absorption spectroscopy in the visible ultraviolet spectral region. Polyaniline is a popular option because of its environmental stability. The goal of this research is to create novel polymer materials with improved conductivity for usage in electrical devices. Polyaniline in base and doped forms were analysed using a variety of reaction times at pilot sizes, allowing for the detection of significant structural, morphological, and other variations. As shown by a comparison of Raman spectroscopy, the doping structure for PAni-DBSA may be deduced from an increase in the polaronic-associated 890 and 1,343 cm1 bands and a decrease in the 1,502 cm1 band (which suggests a break in the C=N bond).

## REFERENCE

[1] Soumen Giri et.al "Preparation and Characterization of the Cobalt Doped Polyaniline/MWCNT Nanocomposites for Supercapacitor Application" DOI:10.5539/jmsr.v1n3p10

[2] Witold Brostow et.al "Flexibility of Polymers Defined and Related to Dynamic Friction" DOI:10.5539/jmsr.v8n3p31

[3] Kingsley Kema Ajekwene et.al "Bulk and nano-structured polyaniline: synthesis, characterization, thermal behaviour and dc conductivity" Vol.6, No.9, September 2018

[4] Sadia, Ameen; Shaheer, M. Akhtar; Minwu, Song; Hyung, Shik Shin (2013): Metal oxide nanomaterials, conducting polymers and their nanocomposites for solar energy. Solar cells - research and application perspectives, edited by Arturo Morales-Acevedo, Publisher: InTech, pp. 203-259

[5] Stejskal, J.; Gilbert, R.G. (2002): Polyaniline: preparation of a conducting polymer. Pure Appl. Chem., 74 (5), pp. 857-867

[6] HuanhuanWang et.al "Polyaniline (PANi) based electrode materials for energy storage and conversion" Volume 1, Issue 3, September 2016,

[7] ZHEFEI LI "SYNTHESIS AND CHARACTERIZATION OF CONDUCTING POLYMER NANOSTRUCTURES AND THEIR APPLICATION IN SENSORS"2010

[8] Mr. Siddhartha Samanta (Ph.D. Nov 2018) Title: Synthesis and Doping of Functional Poly(o-phenylenediamine) for Gas Sensing Application (I was PI)

[9] Selcuk Poyraz "Synthesis and Characterization of Nanostructured Conducting Polymers and Their Composites with Noble Metal Nanoparticles"2010

[10] Grzegorz Kowalsk et.al "Characteristics of Polyaniline Cobalt Supported Catalysts for Epoxidation Reactions" Volume 2014, Article ID 648949, 9 pages

[11] Saiful Izwan Abd Razak et.al "A Review of Electrospun Conductive Polyaniline Based Nanofiber Composites and Blends: Processing Features, Applications, and Future Directions" Volume 2015, Article ID 356286, 19 pages

[12] Sunandana Mandal et.al "Synthesis and Characterization of Polyaniline Based materials: Their biological relevance- An Overview" Int.J.Curr.Microbiol.App.Sci (2017) 6(5): 2309-2321

[13] Maria Alice Carvalho Mazzeu et.al "Structural and Morphological Characteristics of Polyaniline Synthesized in Pilot Scale" Vol.9, No 1, pp.39-47, Jan.-Mar., 2017

[14] Stefanos Mourdikoudis et.al "Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties" DOI: 10.1039/C8NR02278J

[15] P.S.Vijayanand et.al "Facile Preparation And Investigation Of New Electroactive Poly (Aniline-Co-MChloroaniline) Nanocomposites" Volume-8, Issue-2C2, December 2018