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Polypyrrole Nanoparticles Synthesised for Advanced Optoelectronic Applications: Electrical Characterisation

[1]Saba Mohsin Hatata, [2]Dr. Hisham Mohammed Ali Hasan

[1]College of Education; Physics Department, University of Al-Qadisiyah, Diwaniyah , Iraq.
phy.edu.post24.5@qu.edu.iq
[2]College of Education; Physics Department, University of Al-Qadisiyah, 58001 Diwaniyah, P.O. Box 88, Iraq
hisham.hasan@qu.edu.iq

ABSTRACT: polypyrrole (PPy) nanoparticles were prepared using a low-temperature oxidative polymerization process, In this work, the preparation of pure poly pyyrole and poly pyyrole doped with copper oxide and zinc oxide at different concentrations of each doping agent was studied. The effect of different doping concentrations (Cu2O and ZnO) on thermal stability, conductivity, and morphology was observed through electrical conductivity tests , Hall effect .The electrical conductivity and Hall effect characteristics of pure polypyrrole (PPy) and PPy doped with ZnO and Cu2O nanoparticles made utilizing $FeCl_3$ and HNO_3 synthesis techniques were examined in this work.

1-INTRODUCTION:

Before conducting polymers were developed, polymers were thought to be electrical insulators. Conductive or conjugated polymers exhibit special optical and electrical characteristics similar to inorganic semiconductors and metals [1] The conjugated carbon chain's alternating single and double bonds provide highly nonlocal, polarizable, electron-dense π bonds that give them their electrical and optical characteristics[2] Among the desired characteristics of conductive polymers are biocompatibility, electrochemical activity, mechanical flexibility, electrical conductivity, and environmental resilience. Polythiophene (PTH), polypyrrole (PPy), polyfuran (PF), poly (3,4-ethylenedioxythiophene) (PEDOT), poly (para-phenylene) (PPP), polyaniline (PANI), and poly (phenylenevinylene) (PPV) are among a variety of conducting polymers that are primarily used because of their high technological potential. These polymers have been used in the design of rechargeable batteries, sensors, biosensors, solar cells, supercapacitors, and electromagnetic shielding[3]

PPy has been actively utilized in numerous potential applications, including electronic devices, microactuators, antielectrostatic coatings, and biomedical in a variety of organic solvents and aqueous media[4]. It is especially intriguing because of its high stability and conductivity, ease of forming homopolymers and composites, and unique properties like fast charge/discharge process, easy synthesis, high conductivity, flexibility, high energy density, high mass density, and low cost [5].Chemical oxidative polymerization, ultrasonic radiation, electrochemical polymerization, vapour phase polymerization, electrospinning, microemulsion polymerization, mechanochemical polymerization, and photopolymerization are some of the techniques used to create PPy[6]. PPy is a black, powdery material that was first produced by chemically oxidizing a pyrrole monomer with hydrogen peroxide. Polypyrrole has insulating qualities in its undoped pure condition. Nevertheless, it exhibits a constant conductivity of 10–5 S/m[7] . when doped with halogenic electron acceptors like iodine or bromine.Large quantities of PPy fine powders can be produced quickly and easily using chemical oxidative polymerization[8]. Pyrrole (PY) polymerization often happens when chemical oxidants in both aqueous and non-aqueous settings oxidize PY monomer[9]. Numerous reports on the polymerization of PPy using various techniques have been released recently. For instance, Wysocka-Złopa et al.[10] electrochemically polymerized PY in aqueous solutions containing NaClO4 and polymeric or anionic

surfactants such PVP and SDS to create PPy thin films with vertically aligned cone-like features. Maruthapandi et al.[11],[12] used a straightforward one-step chemical process to create PPy Cu2O from carbon dot-initiated PPy and Cu2O composites, The production of two distinct solutions, one containing the monomer and the other the oxidant, is a common procedure for the chemical oxidative polymerization of conductive PPy. These solutions are then combined to start the polymerization. Nevertheless, controlling the homogeneous structure and film thickness of PPy made using this approach is difficult[12].Pyrrole concentrations, doping levels, oxidants, polymerization temperature, impurity presence, and polymerization time all have an impact on PPy electrical conductivity[9]. The impact of several conditions on PPy polymerization has been the subject of numerous reports in recent years. For example, Yusuf et al.[13] investigated the effects of APS and FeCl3 as oxidants on the electrical characteristics of PPy particles. At ambient temperature, they discovered that FeCl3 performs better electrically than APS.

A improved method for producing polypyrrole nanoparticles with adjustable sizes based on reaction circumstances is presented in the paper. The oxidant was added in a single step to an stirred solution. Thus, the effects of various doping (Cu2O and ZnO) and their concentrations on the thermal stability, conductivity, and morphology are examined in this work.

2-EXPERIMENTS:

2-1Materials.

Pyrrole monomer (m PPy) 98% was suppliedby Sigma Aldrich. Anhydrous iron (III) chloride, also called ferric chloride (FeCl3) 98%, and ammonium persulphate (N2H8S2O8) 98% were used as the oxidizing agent and Polyvinylpyrrolidone as stabilizer , (Cu2O ,ZnO) as used as the dopant/surfactant. All of them were supplied by Sigma Aldrich as well. All materials were used as received.

2-1 Synthesizing and Sample Preparation. Polypyrrole (PPy):

2-1-1 Method of preparing polypyrrole nanoparticles using ferric chloride as an oxidant

1- Preparation of pure polypyrrole nanoparticles (Pure PPy)

Pyrrole monomer (0.403 g) was added to 10 ml of deionized water. The beaker was then placed in an ice-filled container and subjected to magnetic stirrer for 4 hours. Afterward, the oxidant, ferric chloride, and the Polyvinylpyrrolidone as stabilizer :(FeCl3 (2.27) g + PVP (0.338 g) were prepared. These were dissolved in 36 ml of water and 4 ml of ethanol. The mixture (oxidant and stabilizer) was then added via a glass burette to the beaker containing the pyrrole monomer by distillation for one hour. The mixture was left on the separator for 24 hours to allow polymerization**.** The mixture was then filtered and washed several times with water and ethanol to remove any remaining residue.

2- Preparation of doped polypyrrole nanoparticles by dopant Cu2O and ZnO by percentages (0.5, 0.8, 1wt%):

A- We dissolve 2 grams of polyvinylpyrrolidone (PVP) as a stabilizer in 200 ml of deionized water in a beaker. The beaker is placed on a magnetic stirrer. During stirring, we add the doped material (Cu_2O or ZnO), copper(II) oxide, or zinc(II) oxide, and continue stirring. The beaker is then placed in a container filled with crushed ice and placed on the magnetic stirrer at 5°C for half an hour. Afterward, 2.5 ml of pyrrole monomer is added drop by drop over 20 minutes, with slow stirring during the addition process, at a temperature of 5°C.

B- We prepare the oxidizer by dissolving 3.5 grams of ammonium persulfate (APS) powder and 3.5 grams of iron chloride ($FeCl_3$) powder in deionized water in a beaker. The beaker is then placed on a stirrer in a container filled with crushed ice at 5°C for half an hour until dissolved. The oxidizer is then added to the mixture. (pyrrole + PVP) is distilled slowly through a glass burette at a low temperature of 5°C. The polymerization process is then carried out on a magnetic stirrer for 6-8 hours. After 24 hours, the mixture is filtered by washing it several times with 5 ml of ethanol and distilled water until the precipitate is removed in a vacuum filtration system.

The polymerization process is repeated with different doping ratios (0.5, 0.8, 1) for Cu_2O and with different doping ratios (0.5, 0.8, 1) for ZnO.

2-1-2- Method of preparing polypyrrole nanoparticles using Nitric Acid (HNO3) as an oxidant:

Place 375 mL of nitric acid (HNO3) in a glass beaker. Then add 0.845 g of pyrrole monomer to the acid by distillation using a pipette. Place the beaker (pyrrole + HNO3) in a container filled with crushed ice at 5°C or lower on a magnetic stirrer for half an hour. Prepare the oxidant by adding 2.85 g of ammonium persulfate (APS) powder to 125 mL of nitric acid (HNO3). Place the oxidant in a glass burette and add it to the beaker (pyrrole + acid) by slow distillation from the burette over two hours. Then allow the polymerization to continue for 6–8 hours in an ice-filled container at a low temperature of 5°C. After 24 hours, filter the mixture using a vacuum filter. Repeat the filtration process several times to remove any sediment.

3-RESULTS AND DISCUSSION:

3-1 Electrical Conductivity Measurement :

Electrical Conductivity (DC) of polypyrrole (PPy) is an important parameter that reflects the efficiency of charge transport within the polymer structure. Pure PPy generally exhibits low electrical conductivity due to the disordered arrangement of polymer chains and the limited number of charge carriers available in the undoped state. This restricts electron movement along the conjugated backbone [14]. The electrical conductivity of polypyrrole (PPy) increases significantly after the doping process. Doping generates charge carriers in the form of polarons and bipolarons within the polymer backbone. These charge carriers become delocalized along the conjugated polymer chains, facilitating charge transport and enhancing the electrical conductivity. In addition, the density and mobility of charge carriers can be controlled through the doping process, leading to a substantial improvement in the electrical performance of conducting polymers such as PPy[15]

The electrical conductivity of polypyrrole depends strongly on dopant concentration, increasing with doping level and showing saturation-like behavior at high concentrations due to limitations in charge transport. [16] [17] The electrical and structural properties of polypyrrole are strongly influenced by doping, where changes in charge carrier concentration and polymer structure affect conductivity [18]

3-1-1 Electrical Conductivity of Pure PPy and Doped (ZnO, Cu2O) Synthesis by FeCl3 as Oxidant :

The investigates of additions of zinc oxide (ZnO) and cuprous oxide (Cu_2O) nanoparticles as pure dopants with different weight percent were carried out. It suggests that the various type of dopants and their concentrations have a large effect on the electrical conductivity of the material. The results indicate that the use of suitable dopants and control of their concentrations might improve the electronic functionality of conducting polymers like polypyrroles.

The key to polypyrrole's conductivity is the linkage of molecules together along the polymer backbone, as well as charge carriers (polarons and bipolarons) incorporated in the structure during the doping process. Metal oxide nanoparticles, such as ZnO and Cu2O, can affect this conductivity through a number of conflicting mechanisms:

1. It may be possible to use nanoparticles as between polymers to enable an electronic transfer of charge carrier between polymer chains and perhaps increase the conductivity of the polymer.
2. Nanoparticles can cause morphological changes that lead to an increase in areas of order—a more conduction-friendly morphologythat is produced by a modification of the morphology and packing of the polymer chains.

3. Nanoparticles can act as scattering centers and charge traps.Nanoparticles can scatter and trap the charge carriers and reduce the mobility.

4- If the doping effect by the nanoparticles could interact with the PPy chain, it could alter the doping level of the PPy chains.The figure 1 shows that pure polypyrrole has relatively low electrical conductivity, as a fundamental state of mind for understanding its potential applications. The effect of doping has been demonstrated on achieving significantly better overall conductivity of these materials that are more appropriate for several electronic and biomedical applications.

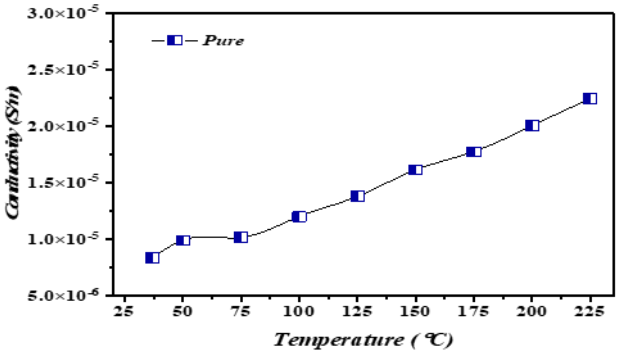

Figure 1: Conductivity of pure polypyrrole.

The doping of polypyrrole with ZnO (Figures 2, 3 and 4 corresponding to 0.5, 0.8 and 1.0 ZnO respectively) presents a rather distinct pattern. The conductivity appears to increase slightly as compared to PPy alone when a small amount of weight fraction of the ZnO nanoparticles, about 0.5 wt%, is added, as is seen in Figure 2. This is likely due to the small size of the ZnO particles facilitating closer contact between the polymer chains which allows electrons to pass more easily through it, creating a more interconnected network.

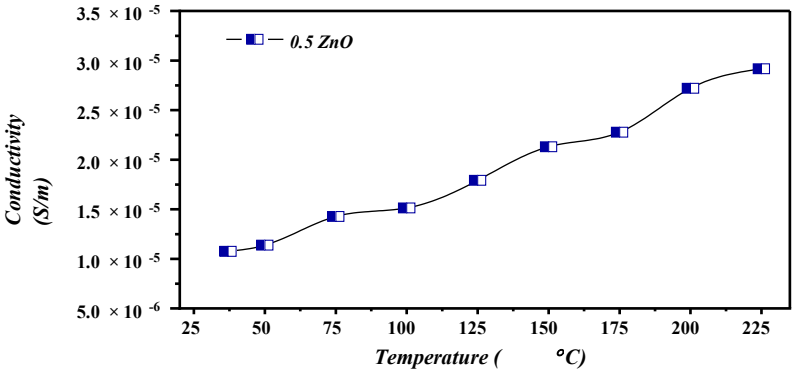

Figure 2: Conductivity of polypyrrole doped by 0.5 % ZnO

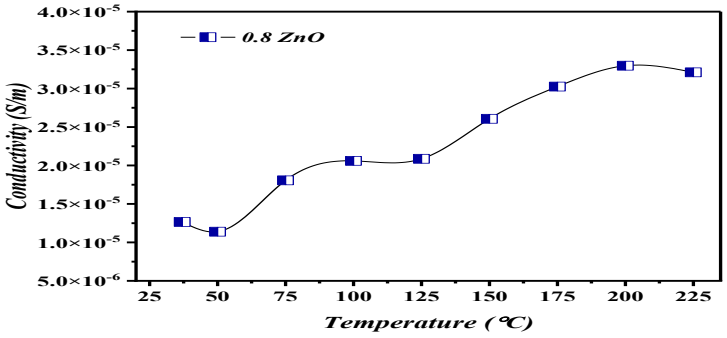

Figure 3: Conductivity of polypyrrole doped by 0.8% ZnO.

The conductivity could change with increasing doping concentration up to 0.8 wt % of ZnO as shown in the first figure and up to 1.0 wt % as shown in the second figure. It may not even reach a minimum value, it may become stable, or even begin to decrease at highest ZnO concentrations. These are a common occurrence with polymer nano composites and typically are

caused by: 1.Have a lot of ZnO, the nanoparticles tend to clump together. These clusters can disrupt the straighforward flow of electricity in the polymer and can get stuck to blocking the charge.

2. Excessive amounts of particles can scatter charge carriers so much that they are unable to travel as far as necessary before hitting another particle. This, in turn, reduces the conductivity of the material in general. there's an optimum amount (subsequently found to range from 0.5 wt% to 0.8 wt%, something in the middle) of puttying with ZnO to achieve its best connectivity properties without having the issues it presents if too much is added because it clumps together.

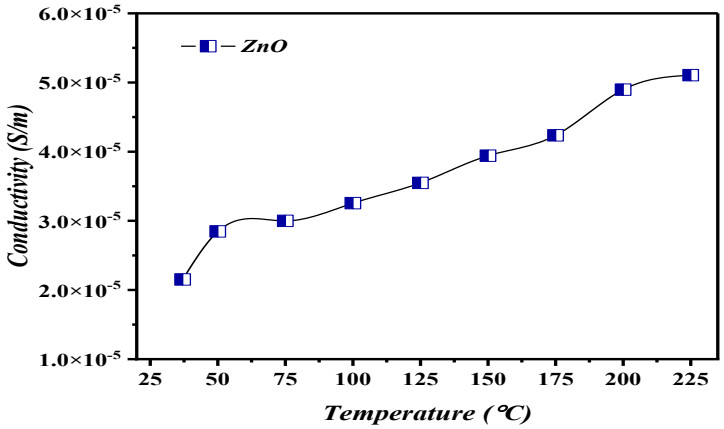

Figure 4: Conductivity of polypyrrole doped by 1.0% ZnO.

With the addition of the Cu_2O nanoparticles, the behavior is different for PPy/Cu_2O nanocomposites in Figures 5-7, compared to the ZnO. This is because Cu_2O is p-type semiconductor and the electronic interaction with the polypyrrole matrix could be different, which is also p-type semiconductor.For the case of the addition of smallest fraction of Cu_2O (0.5wt%, Figure 5), the conductivity has either increased slightly or slightly decreased as compared to the pure polypyrrole. When it decreases, it may indicate that in the first place the Cu_2O is a defect or traps the electrons from conducting electricity properly.

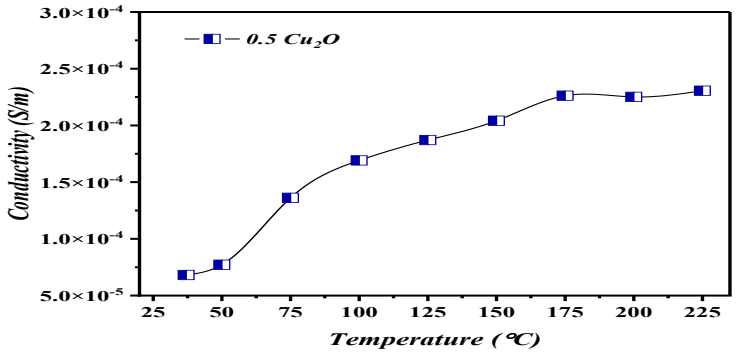

Figure 5: Conductivity of Conductivity of polypyrrole doped by 0.5% Cu_2O.

For Cu_2O concentration >0.8 wt% (Figure 6, bottom), however, significant increase in conductivity has been observed due to sufficient concentration of Cu_2O nanoparticles to establish enough pathways to allow conduction of electrical charge. However, the conductivity may become constant or even decrease as the concentration of Cu_2O (1.0 wt%, Figure 7) becomes the same in the ZnO composites. This may be due to the tendency of the nanoparticles to aggregate and lead to greater scattering of charge carriers. Also, it appears that the percolation threshold for Cu_2O is higher than that of ZnO suggesting that Cu_2O does not interact as well with the polypyrrole in lower concentrations.

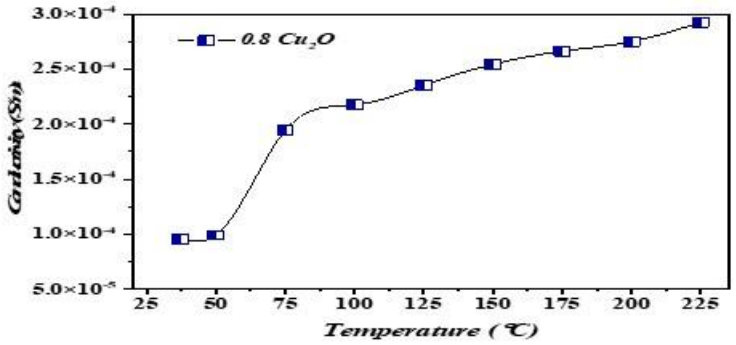

Figure 6: : Conductivity of Conductivity of polypyrrole doped by 0.8% Cu_2O.

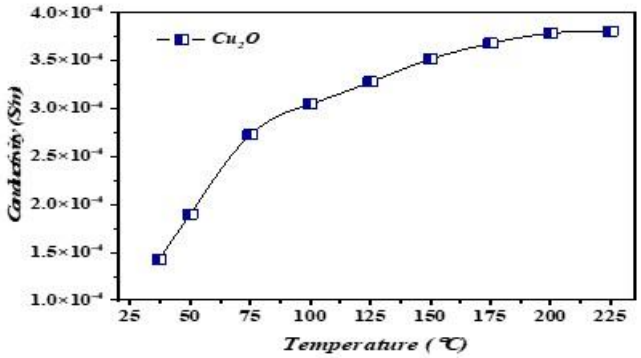

Figure 7: Conductivity of Conductivity of polypyrrole doped by 1.0% Cu_2O.

A comparison between the two material ZnO and Cu_2O would reveal the importance of chemical doping of the material, ZnO being better in this regard at lower concentrations, and thus probably fitting better or having a stronger electronic connection with the polypyrrole chains. The conductivity is increasing with decreasing amount of ZnO content in the sample with respect to Cu_2O content. The results indicate that the main effect of the addition of ZnO was a decrease in the lattice resistance of conducting jump from the polypyrrole chains to the particles. Alternatively, Cu_2O may be more involved in the end and it may require a higher level of concentration to be useful at bridging sites initially but have some ability to trap charges more readily at the end when necessary. The maximum conductivity obtained by using ZnO specimen is probably more than Cu_2O specimen, and also at lower amount of fillers. This means that the electrical conductivity in the polypyrrole nanocomposites is more likely to be achieved using ZnO as it is under the conditions employed.

3-1-2 Electrical Conductivity of pure PPy Synthesis byHNO3 acid as Oxidant

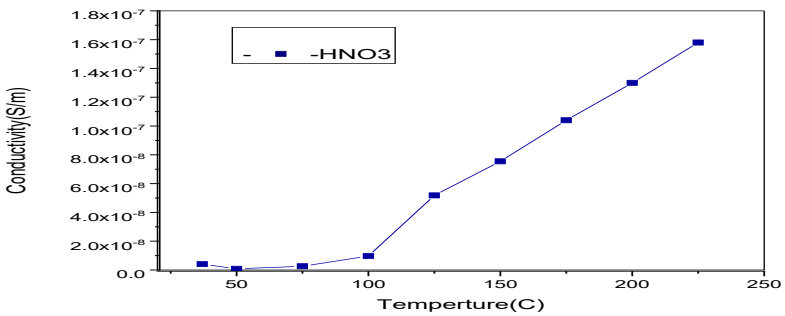

Figure 8: Conductivity of polypyrrole nanoparticles synthesis by nitric acid method polypyrrole (HNO3)

The electric conductivity properties of polypyrrole (PPy) nanoparticles prepared by nitric acid (HNO_3) method reveals an outstanding semiconducting behavior with an increasing trend in conductivity with the rise of temperature, as seen in Figure 8

This behavior is typical for conducting polymers and indicates thermally activated charge transport. The conductivity increased from about 4.09×10^{-10} at 37°C to 1.58×10^{-7} S/cm at 225°C. This large increase of nearly three orders of magnitude confirms that the charge carriers gain sufficient thermal energy at higher temperatures, allowing them to hop more easily between localized states in the polymer chains[19]. The conductivity-temperature dependence can be explained using the thermally activated transport mechanism described by the Arrhenius relation[20]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where:σ = electrical conductivity,

σ_0 = pre-exponential factor,

- E_a = activation energy,
- k_B = Boltzmann's constant,
- T= absolute temperature.

The fact that conductivity increases with temperature indicates that the conduction in the PPy nanoparticles is dominated by hopping conduction of localized polarons/bipolarons along the polymer backbone. Charge transport in conducting polymers like polypyrrole is strongly affected by structural disorder, grain boundaries and chain defects[21]. At low temperatures, carrier hopping between conducting segments is suppressed as the carriers are trapped in localized states. With increasing temperature, thermal activation allows the charge carriers to hop over potential barriers and onto neighboring conducting segments. Thermal conductivity also tells us that nitric acid is successfully doping our polymer during synthesis[22]. Because HNO3 can protonate and oxidize the PPy backbone, it leaves behind counterions that act as positive charge carriers. These charges promote formation of polarons/bipolarons which are responsible for the charge transport. Increasing temperature therefore increases both the carrier mobility and the probability of hopping. The fact that the sample displays a gradual change in conductivity vs temperature with no sharp features indicates that the as-synthesized PPy nanoparticles are thermally stable over the measured temperature range. In other words, no phase transitions or degradations are occuring as you heat your sample. This behavior is typical of amorphous/conformationally disordered conducting polymers[23]. An activation energy can be extracted from the Arrhenius plot of your data. From yours, E a ≈0.45 eV. This value lies in the range for conducting polypyrrole systems as are often encountered. You are thus confirmed to have some semiconducting behavior as shown by your activation energy. In addition, the increased conductivity at higher temperature may be coupled with:

1. Increased segmental motion of polymer chains.
2. Improved overlap of π-electron orbitals.
3. Reduction in carrier trapping effects.
4. Enhanced inter-particle charge transfer between nanoparticles.

3-2 Hall effect Measurement :

Because of the information that may be collected, including Hall voltage, the kind of conductivity, carrier density, and mobility, Hall effect measurements are crucial for characterizing semiconductor materials. The nature, structure, and purity of the material all have a significant impact on mobility. Charge transport, crystallinity, and shape typically influence the charge carrier mobility in conducting polymers. Additionally, a high degree of disorder and a high density of chemical impurities are typically blamed for the low Hall mobility values in polymer materials[32].

3-2-1 Hall Effect Analysis: Undoped Ppy (synthesis by FeCl3 method) and doped ppy by ZnO and Cu2O:

The type, concentration, mobility, and conductivity of charge carriers in conducting polymers are all determined using Hall effect measurements. These characteristics are heavily impacted by the manufacturing process and the addition of inorganic dopants like ZnO and Cu_2O in polypyrrole (PPy). Dopants effects on electrical transport channels and the function of polarons and bipolarons in conduction may be evaluated using the data collected. The addition of inorganic nanoparticles can change the charge carrier density, mobility, and conduction type of conducting polymers like polypyrrole (PPy). The Hall effect characteristics of undoped PPy and PPy doped with different concentrations of ZnO and Cu_2O nanoparticles were methodically examined in this work. The findings show notable patterns in carrier type, concentration, resistivity, and mobility that are dependent on both dopant and concentration. These may be explained by a mix of defect chemistry, percolation theory, and doping processes. Hall effect calculations shows in Table.

Table : Hall effect calculations for undoped and doped nano particle polypyrrole.

Sample	Carrier concentration n $(cm)^{-3}$	Hall coefficient R_H $(cm^{-3}C^{-1})$	Conductivity σ(S/cm)	Mobility (μ) $(cm^2V^{-1}s^{-1})$	Type
Undoped Ppy (synthesis by $FeCl_3$ method)	$1.75x10^{+17}$	$3.56x10^{+01}$	$4.05x10^{-01}$	$1.44x10^{+01}$	P
Ppy dopant 0.5wt% ZnO	$-3.81x10^{+15}$	$-1.64x10^{+03}$	$3.38x10^{-01}$	$5.53x10^{+02}$	N
Ppy dopant 0.8wt% ZnO	$-6.71x10^{+15}$	$-9.31x10^{+02}$	$3.11x10^{-01}$	$2.89x10^{+02}$	N
Ppy dopant 1.0wt% ZnO	$9.14x10^{+14}$	$6.83x10^{+03}$	$5.17x10^{-01}$	$3.53x10^{+03}$	P
Ppy dopant 0.5wt% Cu_2O	$-4.00x10^{+15}$	$-1.56x10^{+03}$	$3.05x10^{-01}$	$4.75\ x10^{+02}$	N
Ppy dopant 0.8wt% Cu_2O	$-3.63\ x10^{+15}$	$-1.72\ x10^{+03}$	$3.46\ x10^{-01}$	$5.95\ x10^{+02}$	N
Ppy dopant 1.0wt% Cu_2O	$9.80\ x10^{+14}$	$6.37\ x10^{+03}$	$3.72\ x10^{-01}$	$2.37\ x10^{+03}$	P

Undoped PPy produced by the $FeCl_3$ technique showed p-type conductivity, which is in line with earlier findings that oxidative polymerization results in hole-dominated transport because polaronic/bipolaronic states are formed [24]. The samples doped with 0.5 and 0.8 wt% ZnO or Cu2O became n-type when doped with just 0.5 or 0.8 wt%, while they were p-type at 1.0 wt%[33,34].This non-monotonic trend implies a complicated interaction between the electrical structure of the polymer and dopant-induced defect levels. ZnO and Cu_2O nanoparticles introduce shallow donor states close to the conduction band at low doping levels (≤0.8 wt%), hence donating electrons to the PPy matrix and raising Fermi levels, This agree with ZnO and Cu_2O's recognized n-type character in bulk [25]. At higher doping concentrations (1.0 wt%), the increased density of dopant particles case the interfacial charge transfer in the opposite direction. This could be because the polymer starts injecting holes into localized states on the nanoparticles or because p-n junctions form at the polymer–particle interface. In same way the carrier-type transitions have been seen in hybrid organic–inorganic systems, and they are frequently explained by conflicting trapping and doping processes[26,27, 28]

The carrier concentration (n) is a parameter that directly influences the electrical conductivity of materials. In this work, Hall effect measurements reveal how doping polypyrrole (PPy) with ZnO and Cu_2O nanoparticles affect the free charge carrier density, providing insight into the doping efficiency and electronic interactions in these hybrid systems[29]

P-type conduction is confirmed by the undoped PPy's carrier concentration of 1.75 × 10^17 cm^{-3}, positive Hall coefficient of 35.6 cm^3C^{-1}, and mobility of 14.4 $cm^2V^{-1}s^{-1}$. $FeCl_3$ produces intrinsic p-doping through the generation of polarons and bipolarons, which is characteristic for polypyrrole produced by oxidative polymerization. The modest carrier density suggests that hole transport along the conjugated backbone with little delocalization controls conduction[30]

The carrier concentration's sign and magnitude are significantly changed when PPy is doped with ZnO. The material becomes n-type at 0.5 weight percent ZnO, with mobility of 553 $cm^2V^{-1}s^{-1}$ and n (-3.81×10^{15} cm^{-3}). Strong electron transport from ZnO to the PPy matrix is suggested by this p-type to n-type inversion. N stays negative (-6.71×10^{15} cm^{-3}) when doping rises to 0.8 wt%, while mobility falls as a result of increased interface scattering and dopant aggregation. The carrier type reverses to p-type (n = 9.14×10^{14} cm^{-3}) at 1.0 wt%, accompanied by an extremely high mobility (3530 $cm^2V^{-1}s^{-1}$). At increasing dopant loadings, competition between charge transfer, carrier trapping, and microstructural rearrangement is reflected in this non-linear behavior[31,32] Cu_2O doping shows comparable patterns. With n (-4.00×10^{15} cm^{-3} and mobility of 475 $cm^2V^{-1}s^{-1}$, the PPy becomes n-type at 0.5 wt%, suggesting significant electron-donor behavior of Cu_2O. At 0.8 weight percent, mobility rises to 595 $cm^2V^{-1}s^{-1}$, indicating better dispersion and less scattering, while n stays negative (-3.63×10^{15} cm^{-3}). The carrier type returns to p-type (n = 9.80×10^{14} cm^{-3}) with strong mobility (2370 $cm^2V^{-1}s^{-1}$) at 1.0 wt%, which is compatible with structural rearrangement and restored dominance of PPy's intrinsic hole conduction routes [33, 34,35]ZnO and Cu_2O both cause a p → n → p transition in PPy, indicating that metal-oxide doping could greatly change the polymer's electrical characteristics, charge-transfer interactions are responsible for the severe suppression of hole density at low dopant levels, whereas percolation effects and dopant-induced structural rearrangement are responsible for the return of p-type behavior at high loadings. Mobilities rise sharply with doping, suggesting that better microstructural organization, rather than carrier density, increasingly controls transport, these demonstrate that metal-oxide nanoparticles are useful modifiers for modifying polypyrrole's electrical transport characteristics for cutting-edge electronic, sensing, and energy applications [35 36].Electrical conductivity shows relatively little variation (0.30–0.51 S/cm) among all specimens, even with considerable changes in n. This suggests that the electrical conductivity of PPy is not solely dependent on carrier concentration. On the other hand, it is greatly influenced by mobility and transport processes based on hopping, which are specific to conducting polymers[46], reaching 3530 cm2/V·s with doping.This improvement suggests better microstructural arrangement, less scattering, and the development of pathways for efficient transport[37] Elevated mobility can offset a low concentration of charge carriers, thereby maintaining conductivity. PPy experiences full carrier inversion from p-type to n-type at 0.5 weight percent ZnO, with RH = -1.64×10^3 cm^3/C and n = -3.81×10^{11} cm^{-3}. Strong electron donation from ZnO to the PPy matrix is shown. A significant improvement in mobility to 553 $cm^2/V{\cdot}s$ indicates better charge transport channels [38]. The material is still n-type at 0.8 weight percent ZnO (n = -6.71×10^{11} cm^{-3}), but mobility drops to 289 $cm^2/V{\cdot}s$ because of enhanced scattering brought on by dopant aggregation. ZnO-doped PPy exhibits extraordinarily high mobility (3530 $cm^2/V{\cdot}s$) and recovers to p-type behavior (n = $+9.14 \times 10^{11}$ cm^{-3}) at 1.0 weight percent. This reversal is associated with microstructural reordering, in which hole dominance is restored by excessive dopant, which lowers electron transfer efficiency [39 ,40] .Cu2O exhibits comparable patterns to ZnO, although it donates electrons more strongly. At 0.5 weight percent, n equal (-4.00×10^{11} cm^{-3}) and RH is (-1.56×10^3 cm^3/C), indicating n-type conduction. Mobility increases to 475 $cm^2/V{\cdot}s$. Mobility improves to 595 $cm^2/V{\cdot}s$ at 0.8 weight percent, but n stays negative. The sample exhibits excellent mobility (2370 $cm^2/V{\cdot}s$) and recovers to p-type (n = $+9.80 \times 10^{11}$ cm^{-3}) at 1.0 weight percent Cu_2O, showing structural rearrangement that restores hole transport[41,19]

3-2-2 Hall Effect Analysis :Nano Particle Polypyrrole Ppy (synthesis by Acid HNO3 method) :

Acid-mediated pathway-produced polypyrrole (PPy) often exhibits distinct structural and electrical characteristics[42]. The Hall effect data for PPy nanoparticles produced by the acid method, with particular focus on carrier concentration, mobility, resistivity, and conduction type. The results clarify the charge transport mechanisms operating in this kind of PPy and provide a baseline for comparison with doped or differently produced variants.[43]

1.41×10^{18}cm−3 is the carrier concentration. This value is comparatively high for undoped PPy, indicating that a larger density of charge carriers may be introduced via the acid production process, either as a result of inherent structural order or protonation.[44]The conductivity is 9.52×10−3 (Ω·cm)−1, the resistivity ϱ = 1.05×102 ×·cm, and the sheet resistance Rs is 5.25×105Ω. For PPy, this conductivity is modest, suggesting that mobility may be restricted despite a high carrier

concentration. When it comes to Carrier Mobility μ≈4.21×10−2cm2/V·s, this poor mobility is typical of disordered conducting polymers, where charge transfer takes place by hopping between localized states. 4.42×10−3cm3/C is the Hall Coefficient (RH). P-type conduction is confirmed by the positive sign of RH, which is in line with hole-dominated transport in PPy.[45]The calculated carrier concentration (1.41×1018 cm−3) is significantly greater than what is usually reported for oxidatively produced undoped PPy (normally 1016 to 1017 cm−3). This improvement might be explained by the PPy backbone being protonated during acid production, which raises the density of polaronic and bipolaronic charge carriers. Acid-mediated polymerization and improved chain alignment may encourage more regular chain packing, improving carrier delocalization and ππ-conjugation. Decreased defect density: The development of carbonyl or other trap states that lower effective carrier density may be suppressed via the acid pathway.[46] With a conductivity value of (σ≈10−2 Ω−1cm−1), mobility is the limiting constraint. The poor mobility (μ≈4.2×10−2 cm2/V·s) .is characteristic of hopping conduction in disordered conducting polymers, where charge transport is limited by localized trap states, structural disorder, and inter-chain hopping barriers.[39]

4- CONCLUSIONS :

Using techniques that involved HNO_3 and $FeCl_3$, polypyrrole (PPy) nanoparticles were successfully manufactured oxidative polymerization. Using DC electrical conductivity and Hall effect measurements, the influence of doping with Cu_2O and ZnO nanoparticles on PPy's electrical transport parameters was investigated in depth. All samples tested were semiconductors, according to conductivity tests. The results showed that, upon the use of nitric acid, charge transport is thermally activated and occurs via jumping pathways, including polarons and bipolarons, with electrical conductivity increasing with temperature. The addition of metal oxide nanoparticles greatly affected the electrical properties of PPy. In particular, the introduction of ZnO and Cu_2O dopants enhanced the charge transport by affecting charge concentration, charge mobility, and the charge transfer at interfaces in the polymer. It was found that an optimum concentration of the dopants was present above which the doping level would cause a scattering of the carriers and aggregation of the nanoparticle, both of which would impact conductivity. Undoped PPy prepared through the $FeCl_3$ process prepared using low-temperature was found to be p-type conductive based on the results of hall effect studies, where charge transfer was found in the form of holes. Interesting: although the ntype conductivity behavior can be recovered by increasing the dopant loading (1.0 wt%) the ntype conductivity can be obtained by reducing the loading (0.5 and 0.8 wt%) of the ZnO and Cu2O dopants respectively. This is a carriertype inversion indicating that the polymer chains and the metal oxide nanoparticles possess s trong electric connection; this significantly changes the charge transport pathways.

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