ORIGINAL RESEARCH PAPER | Volume - 13 | Issue - 08 | August - 2024 | PRINT ISSN No. 2277 - 8179 | DOI : 10.36106/ijsr

INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCH

INVESTIGATING THE ROLE OF FE ON STRUCTURAL, MORPHOLOGICAL AND ELECTRICAL CHARACTERISTICS OF POLYPYRROLE NANOPARTICLES

Chemistry

Raju P. Tandel S.d.s.m. Dandekar College, Palghar, Maharashtra, India

Vinod S. More* G.e.s.s N. B. Mehta Science College, Bordi, Dahanu, Palghar, Maharashtra, India *Corresponding Author

T. N. Ghorude G.e.s.s N. B. Mehta Science College, Bordi, Dahanu, Palghar, Maharashtra, India

ABSTRACT

Polypyrrole (PPy) is immensely popular especially among conducting polymers since it has excellent electrical conductivity. Polypyrrole (PPy) nanoparticles were synthesized using chemical oxidative polymerization using ferric chloride ($FeCl_3$) as an oxidizing agent. The synthesis was performed in from 0.5 to 2.0 molar ratios (M.R.). To verify polymer manufacturing, the resultant PPy nanoparticles undergo comprehensive analysis using methods like SEM, XRD, and FTIR. The two-probe approach was used to measure electrical conductivity. The results of the comparative investigation showed that the nanoparticles with the best electrical conductivity were those that were manufactured at a M.R. of 1.0. Because of their increased conductivity, PPy nanoparticles with a M.R. of 1.0 appear to be excellent for use in sensor technologies.

KEYWORDS

Polypyrrole, PPy, FeCl3, Sensor

INTRODUCTION

conducting polymers are a remarkable class of organic polymers with a unique capability of conducting electricity [1]. Conducting polymers have electrical characteristics similar to those of metals or semiconductors, in contrast to conventional polymers, which are generally insulators. Its conjugated π-electron structures, wherein single bonds that alternate with double bonds form a channel for delocalization of electrons along the polymer backbone, are responsible for their exceptional electrical conductivity[2], [3].

When polyacetylene was doped with iodine, researchers Alan J. Heeger, Alan MacDiarmid, and Hideki Shirakawa showed that polyacetylene significantly boosted its electrical conductivity [4]. This led to the discovery of conducting polymers. They were awarded the 2000 Chemistry Nobel Prize for their pioneering study, which also opened the door for profound investigations of various other conducting polymers like polyaniline, polypyrrole, and polythiophene [5].

Conducting polymers are beneficial for a variety of applications because of their low weight, adaptability, and simple manufacturing. These include applications in energy storage systems, sensors, electronic gadgets, and even medical equipment. Their capacity to fuse the electrical and mechanical characteristics of metals and polymers creates novel opportunities across a range of sectors [6].

Polypyrrole (PPy) is a unique and adaptable conducting polymer which belongs to the intrinsically conducting polymer family, also known as 'synthetic metals' [7]. It is synthesized by oxidatively polymerizing pyrrole monomers to create a polymer that encourages electrical conductivity and has a conjugated π-electron structure [8]. The advantages of polypyrrole are its easy production, environmental stability, and high electrical conductivity. It usually takes the form of a black powder and is insoluble in the majority of conventional solvents, which makes processing difficult. Despite these difficulties, its inherent qualities render it extremely desirable for a wide range of high-tech uses, such as biomedical devices [9], electronics, and sensors [10].

Polypyrrole (PPy) is a common conducting polymer owing to its simplicity of manufacture and high electrical conductivity [11]. Its structure can be precisely controlled during synthesis using either electrochemical polymerization or simple chemical oxidative polymerization. Because of its well-known stability in both air and moisture, PPy is perfect for use in severe situations. Functional adaptability is yet another significant benefit of PPy. It may be readily changed with different chemical groups to create composites containing metals as well as carbon nanomaterials, which enables the creation of materials with specialized properties for use in particular applications. Because of its biocompatibility and general non-toxicity, it can be used in biomedical applications such as drug delivery systems and biosensors [12], [13].

PPy is also affordable and scalable, with its monomer, pyrrole, being readily available. PPy is an attractive option for commercial applications and large-scale production due to its cost advantage. Because of its high sensitivity and selectivity, PPy is an excellent sensor technology for detecting a variety of chemical and biological chemicals, such as gases and biomolecules. Its mechanical flexibility makes it possible to develop wearable and flexible sensors, which are crucial to modern technology and healthcare [13], [14].

In these research work, we are synthesizing PPy with various amount of $FeCl_3$ to obtain Oxidant to Monomer molar ratio (M.R.) ranging from 0.5 to 2.0. Additionally these nanoparticles charcaterized by various charcaterization techniques such as Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) to study the structural, morphological and electrical characteristics. Further, we incorporated these nanoparticles to make pallets of diameter 1 cm using pelletizer. The electrical conductivity of these pellets were determined using two probe method. Comparative study of these nanoparticle showed the impact of amount of Fe on the basic characteristics of PPy. This makes it suitable for fabrication of electrical devices and sensor.

MATERIALS AND METHODS:

Materials:

Pyrole (C_4H_5N), the monomer, was purchased from Spectrochem Pvt. Ltd. in analytical reagent (AR) grade. It was then kept in a dark, temperature-controlled environment at 5°C under close monitoring. The oxidant used was iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), which is also of analytical grade.

Pyrrole was distilled at low pressure before use to get rid of any possible contaminants. Double distilled water was used to prepare the $FeCl_3{\cdot}6H_2O$ solution and the polypyrrole.

Methods:

Synthesis of PPy Samples:

Ppy was synthesized using the chemical oxidative polymerization method[15]. Pyrrole was the monomer and $FeCl_3$ was the oxidant in this reaction. First, different quantities of $FeCl_3$ were added to 1 mL of 1 M aqueous pyrrole solution in order to get Oxidant to Monomer ratios (M.R.) of 0.5, 1.0, 1.5, and 2.0. Using a magnetic stirrer, the mixture was constantly stirred for six hours at a regulated temperature of near 0°C. After that, the mixture was left alone for an entire night so that polymerization could occur.

After the reaction was finished, PPy precipitate turned black. Vacuum filtration was used to separate the precipitate, which was then dried and repeatedly cleaned with double distilled water to get rid of impurities. The end result was a PPy nanoparticle powder, which was then used for characterisation. The PPy synthesis reaction from pyrrole monomer [16] is shown in the fig.1.

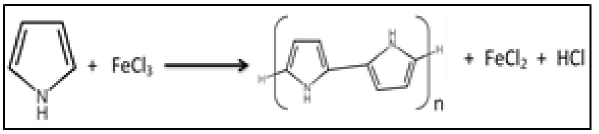

Fig.1 : Chemical Reaction of synthesis of polypyrrole from pyrrole

Characterization:

The study involved a number of examinations for the synthesized samples. The FEI Quanta 200 Scanning Electron Microscope (SEM) was used to examine surface morphological features. Using a Bruker ALPHA II FTIR Spectrometer, the Attenuated Total Reflectance (ATR) method was used to obtain infrared (IR) spectra. We used a PANalytical instrument for XRD characterization of our polypyrrole-based materials. The dc electrical conductivity was assessed using the two-probe method. These measurements shed light on the properties of the samples with varying iron chloride concentrations. Furthermore, samples with the greatest and most consistent conductivity were appropriate for sensor fabrication.

RESULT AND DISCUSSION:

Pyrrole undergoes polymerization in order to produce polypyrrole (PPy) nanoparticle. For many kinds of characterisation and analysis, these nanoparticles were utilized.

SEM analysis:

SEM study highlights unique characteristics of PPy nanoparticles that are frequently utilized in materials science. As shown in Fig.2, PPy is often synthesized to produce nanoparticles with a distinctive spherical form. It's interesting to note that PPy with notable globular structures are formed when the polymerization process is carried out at low temperatures, a method frequently used to customize polymer characteristics for electrical applications. The generate globules, which appear nearly spherical and densely packed, have an average size of 70–90 nm when iron chloride is utilized in the polymerization process. As the level of Fe rises to a higher M.R., the spherical shape of the nanoparticles becomes apparent. These granules appear to develop on top of one another within M.R. 0.5 and 1.0, creating a continuous structure. This kind of morphology is useful, especially for fabrication of effective sensor [17].

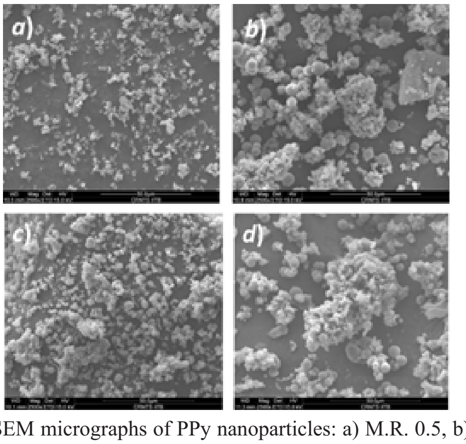

Fig.2: SEM micrographs of PPy nanoparticles: a) M.R. 0.5, b) M.R. 1.0, c) M.R. 1.5, d) M.R. 2.0

FTIR Analysis:

Fig.3 illustrates the FTIR spectra of PPy. It shows a distinctive peak in the 3421–3292 cm−1 range, which is indicative of the O–H stretching vibration [16].

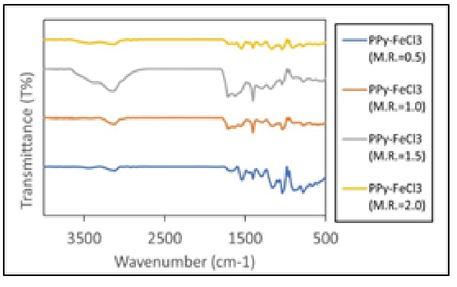

Fig.3: FTIR spectra of PPy nanoparticles at various M.R. (0.5 to 2.0)

Furthermore, it is possible to trace the peak found at 2774-2958 cm−1 to the C-H stretching vibration. The stretching vibration of the carbonyl group, which results from the partial oxidation of the alcohol to the carboxyl group, is shown by the absorption peak, which is roughly located at 1538 cm−1. For M.R. of 1.0 and 1.5 in the case of PPy, greater peak values are noted in the range of 1706-1122 cm−1. This is explained by the chemical oxidative polymerization process that takes place when water is present. The effective polymerization of PPy nanoparticles is confirmed by the characteristic peaks observed in the spectrum [18].

XRD analysis:

Fig.4 shows the XRD of PPy nanoparticles at different M.R.ratios. The nature of all these sample shows amorphous characters with some crystallinity regions. The most prominent broad peak shown at about 2 25^{0}. This gives the confirmation of existence of PPy in the sample. The impact of Fe is shown in the XRD pattern that it slightly changes its intensity [19].

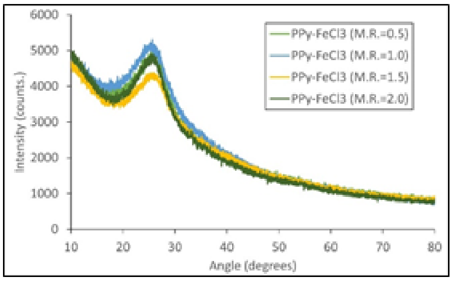

Fig.4: XRD spectra of PPy nanoparticles at various M.R. (0.5 to 2.0)

Dc electrical conductivity measurement:

This approach includes sandwiching a pellet within two probes with a surface area of 1 cm^2. The graph of I-V characteristics shown in Fig.5. We calculated the sample's electrical conductivity at temperatures ranging from 30 ^{0}C to 50 ^{0}C using the formula [20],

Conductivity, $\sigma = \frac{I}{V}\frac{t}{A} = \frac{t}{R \times A}$

Where, V = voltage applied, t = Thickness of the sample, I = current, R= resistance of the sample = $\frac{V}{I}$, A = Cross-sectional Area of the sample in contact with the probe.

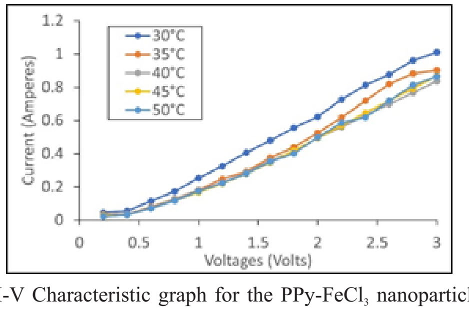

Fig.5: I-V Characteristic graph for the PPy-$FeCl_3$ nanoparticles for M.R.= 1.0 at different temperatures

Table: Electrical conductivities of Ppy samples at various concentration of $FeCl_3$

Monomer-oxidant	Molar ratio (M.R.) Oxidant:Monomer	Conductivity ($S\text{-}cm^{-1}$)
PPy-$FeCl_3$	0.5	3×10^{-3}
PPy-$FeCl_3$	1.0	3.36
PPy-$FeCl_3$	1.5	9×10^{-1}
PPy-$FeCl_3$	2.0	12×10^{-2}

The electrical conductivities for different PPy sample is illustrated in the Table above. The electrical conductivity for the sample of M.R. 1.0 is much higher of about 3.36 S/cm shows stable conductivity at various temperatures, which make this sample suitable for gas sensing applications.

CONCLUSION:

We successfully synthesized polypyrrole (PPy) with varying concentrations of $FeCl_3$ in this study, and we used SEM, XRD, and FTIR to characterize the materials that resulted. SEM analysis showed that the concentration of $FeCl_3$ significantly influenced the spherical morphology of PPy, with distinct structural features emerging at different ratios. XRD patterns indicated changes in crystallinity with varying $FeCl_3$ quantities, highlighting the role of $FeCl_3$ in influencing the molecular arrangement of PPy. FTIR spectroscopy verified the successful synthesis of PPy, showing characteristic peaks of the polymer and its interactions with $FeCl_3$. The sample with the greatest electrical conductivity at room temperature was found to have a molar ratio (M.R.) of 1.0, according to conductivity studies carried out using the two-probe method. The excellent structural organization made possible by the $FeCl_3$ concentration, which encourages effective charge transport via the polymer matrix, is responsible for this increased conductivity. These results imply that the M.R.=1.0 sample is especially well suited for sensor technology since its high conductivity can enhance the sensitivity and response of the sensor.

REFERENCES:

[1] N. K and C. S. Rout, "Conducting polymers: a comprehensive review on recent advances in synthesis, properties and applications," *RSC Adv*, vol. 11, no. 10, pp. 5659–5697, 2021, doi: 10.1039/D0RA07800J.

[2] "Conducting polymers forward," *Nat Mater*, vol. 19, no. 9, pp. 921–921, Sep. 2020, doi: 10.1038/s41563-020-0792-7.

[3] C. I. Awuzie, "Conducting Polymers," *Mater Today Proc*, vol. 4, no. 4, pp. 5721–5726, 2017, doi: 10.1016/j.matpr.2017.06.036.

[4] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, "Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH) x," *J Chem Soc Chem Commun*, no. 16, p. 578, 1977, doi: 10.1039/c39770000578.

[5] "The Nobel Prize in Chemistry 2000 - NobelPrize.org." Accessed: Jul. 23, 2024. [Online]. Available: https://www.nobelprize.org/prizes/chemistry/2000/summary/

[6] S. Shahabuddin, N. A. Mazlan, S. N. A. Baharin, and K. P. Sambasevam, "Introduction to Conducting Polymers," 2021, pp. 1–18. doi: 10.1007/978-3-030-62090-5_1.

[7] A. Marutaphan and C. Wongchoosuk, "SCC-DFTB Study on Structure, Electronic and Sensing Properties of Polypyrrole," *J Phys Conf Ser*, vol. 901, p. 012079, Sep. 2017, doi: 10.1088/1742-6596/901/1/012079.

[8] D. D. Ateh, H. A. Navsaria, and P. Vadgama, "Polypyrrole-based conducting polymers and interactions with biological tissues," Dec. 22, 2006, *Royal Society*. doi: 10.1098/rsif.2006.0141.

[9] Z. Mao Jifu and Zhang, "Polypyrrole as Electrically Conductive Biomaterials: Synthesis, Biofunctionalization, Potential Applications and Challenges," in *Cutting-Edge Enabling Technologies for Regenerative Medicine*, C. H. and K. I. K. and K. G. Chun Heung Jae and Park, Ed., Singapore: Springer Singapore, 2018, pp. 347–370. doi: 10.1007/978-981-13-0950-2_18.

[10] A. G. Anil, S. Singh, J. Joji, J. Singh, and P. C. Ramamurthy, "Conducting Polymer Based Sensor," in *Encyclopedia of Materials: Electronics*, Elsevier, 2023, pp. 28–35. doi: 10.1016/B978-0-12-819728-8.00125-X.

[11] N. Singh, "Polypyrrole-based emerging and futuristic hybrid nanocomposites," *Polymer Bulletin*, vol. 79, no. 9, pp. 6929–7007, Sep. 2022, doi: 10.1007/s00289-021-03840-5.

[12] I. Sapurina, C. Bubulinca, M. Trchová, J. Prokeš, and J. Stejskal, "Conducting polypyrrole and polypyrrole/manganese dioxide composites prepared with a solid sacrificial oxidant of pyrrole," *Synth Met*, vol. 278, p. 116807, Aug. 2021, doi: 10.1016/j.synthmet.2021.116807.

[13] S. Khamlich *et al.*, "Polypyrrole/graphene nanocomposite: High conductivity and low percolation threshold," *Synth Met*, vol. 198, pp. 101–106, 2014, doi: 10.1016/j.synthmet.2014.10.004.

[14] P. Chen *et al.*, "Highly selective NH3 gas sensor based on polypyrrole/Ti3C2Tx nanocomposites operating at room temperature," *Journal of Materials Science: Materials in Electronics*, vol. 33, no. 9, pp. 6168–6177, Mar. 2022, doi: 10.1007/s10854-022-07792-y.

[15] F. N. Diauudin *et al.*, "Preparation and Characterisation of Polypyrrole-Iron Oxyhydroxide Nanocomposite as Sensing Material," *Advances in Materials Science and Engineering*, vol. 2020, 2020, doi: 10.1155/2020/8762969.

[16] A. Yussuf, M. Al-Saleh, S. Al-Enezi, and G. Abraham, "Synthesis and Characterization of Conductive Polypyrrole: The Influence of the Oxidants and Monomer on the Electrical, Thermal, and Morphological Properties," *Int J Polym Sci*, vol. 2018, 2018, doi: 10.1155/2018/4191747.

[17] Y. Sood, V. S. Pawar, H. Mudila, and A. Kumar, "Influence of Polypyrrole Morphology on Gas Sensing," in *Journal of Physics: Conference Series*, Institute of Physics, Jun. 2022. doi: 10.1088/1742-6596/2267/1/012050.

[18] R. Ansari, "Polypyrrole Conducting Electroactive Polymers: Synthesis and Stability Studies," *E-Journal of Chemistry*, vol. 3, p. 860413, 2006, doi: 10.1155/2006/860413.

[19] S. B. Pagar, T. N. Ghorude, M. P. Nikolova, and K. SenthilKannan, "Synthesis, physical, chemical, biological, mechanical and electronic studies of polypyrrole (PPy) of versatile scales for electro-mechano, pharmaceutical utilities," *Heliyon*, vol. 9, no. 9, p. e20086, Sep. 2023, doi: 10.1016/j.heliyon.2023.e20086.

[20] J. John and S. Jayalekshmi, "Polypyrrole with appreciable solubility, crystalline order and electrical conductivity synthesized using various dopants appropriate for device applications," *Polymer Bulletin*, vol. 80, no. 6, pp. 6099–6116, Jun. 2023, doi: 10.1007/s00289-022-04354-4.