

Novel Route To Synthesize N Doped (O- Phenylenediamine) Using Various Acids

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Abstract:

A material we set up poly(phenylenediamine) (PoPD) doped with different acids, for instance, hydrochloric, sulfuric, formic, phosphoric, and so on, including an oxidative polymerization procedure with potassium dichromate as an oxidant. FTIR and UV visible spectroscopy were used to characterize the polymer components. In the case of PoPD H_2SO_4 and PoPD H_3PO_4 , the FTIR spectra revealed a shift to bring down wave number, suggesting that the PoPD doping levels in H_2SO_4 and H_3PO_4 are the best. In UV vis spectroscopy, an efficient doping of PoPD in H_3PO_4 was observed. The thermo gravimetric research revealed three stages of degradation (TGA). In H_3PO_4 doped polymer, the second step misery associated with dopant deficit is considered as greater. The electrical conductivity benefits of PoPD H_2SO_4 and PoPD H_3PO_4 are thought to be the highest of all the acids. Poly (o- phenylenediamine) (PoPD) was successfully synthesized in acid by chemical oxidation method using potassium dichromate as an oxidant. The synthesized polymer was characterized using Raman spectroscopy, SEM, XRD and BET surface area. More unevenly dispersed particles of the Poly (o- phenylenediamine) polymer were observed from the SEM images

Keywords: Carbon Derivatives, Electro-chemical Properties, Polyphenylene diamine, Potassium dichromate, UV vis spectroscopy, Fourier transform infrared, solvothermal technique

1. Introduction

In the current time Nitrogen (N) doped polymer composites are more popular because of catalysis, energy reaping gadgets as supercapacitor, Li-particle batteries, sun powered cells, energy unit and oxygen decrease response (ORR) in metal air batteries and deformity designing applications. N doped polymer moieties were altered by utilizing different blend procedures followed by substance shower affidavit (CVD), bend release strategy, solvothermal technique, pyrolysis, plasma treatment. The certification of N doped polymer moieties changed structure, significant disfigurements and morphologies of the models were expected by Use AFM (nuclear power magnifying instrument), TEM (transmission electron magnifying lens) and FEM (channel electron magnifying lens) (SEM) followed by X-shaft photoelectron spectroscopy (XPS) fundamental responsibility. On a fundamental level in view of solitary pair electrons of doped N gave extra bad charges it worked on the particular capacitance of immaculate example favored different electrochemical applications. Primary deformities caused because of N doping may go about as

polarization focuses. The N molecule has greater electro-negativity when contrasted with carbon. Dielectric properties showed expanded dielectric permittivity with decreased misfortune. Gotten results showed N doping is a regulative device to control the dielectric properties. [1] We accentuated in the current audit, blend roots, portrayal procedures and ongoing utilizations of N doped polymer moieties.

Carbon-based nanomaterials have received a lot of attention for their potential to improve a variety of natural, Electrical, and mechanical applications. Since then, their functions and viable makes use of were very well investigated. Because in their thrilling bodily and compound properties, consisting of excessive surface-to-quantity proportion, excessive conductivity, excessive strength, and substance latency, the investigation of molded carbon nano-materials, such as carbon nanotubes (CNTs), has invigorated colossal premium for developing sensors. [2]

The CNTs are pushed up graphene sheet chambers. For a long time, a few scientists worked on these types of materials and accomplished several experiments. Regardless, in 1991, Dr. Ijma was originally identified as CNT. SWCNT is a solitary nonstop wrap graphene sheet with a hexagonal scented ring design. It very well may be climbed in various ways, and SWCNT plans can be isolated into three fundamental sorts: rocker, cruciform, and chiral. MWCNT is made from coaxial SWCNT foil and can be used in a variety of finishes. One example is the alleged herringbone surface, where the graphene layer is located similar to the center of the nanotube. The other is the so-called "bamboo" surface, which has a layer of graphene oriented in the opposite direction of the nanotube pivot. [3]

Flow research is a methodology to explore how CNTs are modified by grip to sidewalls, CNT tips, and mass changes to exploit the appealing properties of CNTs. The qualities of MWCNTs and SWCNTs rely upon the design and surface of the CNTs, yet the fundamental downsides are in their application is the dispersing of the CNTs in different solvents.

The type of deformation caused by the heteroatom has an impact on the type of conduction formed while switching from n-type to p-type transport (N replacement doping) (B replacement of boron in cross section). CNTs have been altered and functionalized for use in gadgets, clinical and biomedical applications, liquid stage responses, power supplies called nano-energy materials, and gas sensors that address dissipating issues and further develop reactivity. For the motivations driving this examination, we will similarly zero in on their drug/promising applications in the organized locale, from building materials to run of the mill materials, electrical stuff to high nano-energy materials. [4]

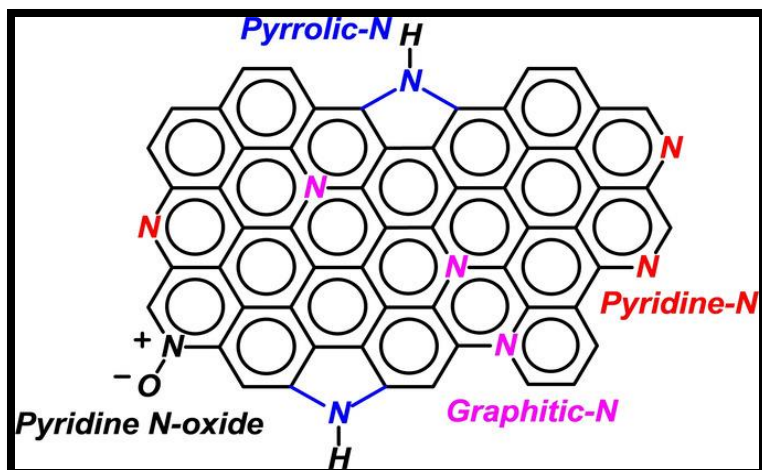


Figure: 1: Nitrogen Doped Carbon Nano Material

O-Phenylenediamine PoPD

It is easy manufacture, good environmental stability, interchangeability of oxidation states, electrical and optical properties, as well as an affordable cost, polyaniline is an essential member of the intrinsically conductive polymers. Aniline derivatives include phenylenediamine (PoPD), but PoPD exhibits distinct characteristics from aniline. Compared to aniline, poly (o-phenylenediamine) exhibits distinct physical characteristics. Diverse industries find use for polyaniline derivatives, such as chelating of heavy metals from industrial waste and the development of microelectronic and electromagnetic shielding and optical systems. Conducting polymer polymerization can be accomplished chemically or electrochemically. In addition to ammonium persulfate and ammonium persulfate, ammonium persulfate can be utilised as chemical oxidising agents. Potassium dichromate was utilised in this study as an oxidising agent in the chemical polymerization of (ophenylenediamine).

2. Background Information

2.1. Essentials of Conducting Polymers

At the factor while one considers polymers, one perhaps imagines ordinary plastics or rubbers, which might be excellent protectors. Indeed, many main polymers had been top notch of their non-conducting systems earlier than their electric residences had been discovered. For example, compound oxidative polymerization of aniline became accounted for via way of means of Lethe by as quickly as 1862. Notwithstanding, it became least difficult following 100 years sometime later, for the length of the 1970s, that Alan J. Heeger, likewise, partners figured out the unreasonable conductivity of polyacetylene. That is the very thing that they found withinside the wake of doping with AsF_5 , the conductivity of cis-polyacetylene has become cycle 220 S/cm at room temperature. From that point forward numerous ordinarily primary polymers with colossal electric and optical homes, for instance, polyaniline (PANI), polythiophene (PT), polypyrene (PPy), and different related substances, had been mixed. These polymers are frequently known as "home grown semiconductors" or "designed metals". [5]

2.2. Band

Materials in truth can normally be characterized into 3 instructions as indicated via way of means of their electric conductivity: separators, semiconductors, and guides. A band version makes experience of why some substances lead electric fee, even as a few don't. As consistent with the band version, the protecting of character atomic digital states can create digital companies. The valence electrons move over to line a valence band, even as electrons withinside the conduction band have better energies, which may be sufficient to permit electrons to ship shamelessly withinside the substances. [6]

The power appraisal among those organizations is known as band empty, through method of method for and monstrous demonstrated as E.g. In steel chiefs, the valence band and the conduction band get over; thus, electrons can circle wholeheartedly in a premise of great charge outlined through method of method for the molecule habitats. The band empty of separators is for the most extreme component uncommonly over the top, bringing roughly a low conductivity at room temperature. On the off danger that the band empty is nearly nothing (e.g., 2 eV), the valence electrons might be empowered into the conduction band through method of method for heat or phonon excitation. [7]

The electrons then develop to be compact, and the material is known as a semiconductor. Along these lines, a fundamental polymer, on the component while in a right oxidized or decreased state, is generally a semiconductor coming roughly from the delayed π -development. The safeguarding of the π -organizations is the valence band, and the π^* -band is the conduction band withinside the primary polymers. Expecting that the band burrow is taken out through method of method for moreover widening the π -development, a coordinating polymer might be pretty much as conductive as steel. [8]

2.3. Doping

Doping is the procedure considered about giving corruptions (dopants) as a way for expanding the conductivity of a material. The doping of coordinating polymers recommends (1) rate move (through method of method for oxidation, p-kind doping or by means of method of method for decline, n-kind doping), (2) the related consideration of a counter molecule for the general unbiasedness, and (3) the simultaneous oversee of build potential. Essential doping might be done falsely or electrochemically. The doping stage is predicated upon the kind of dopant and on its scattering withinside the polymer. P-kind doping, completed through method of method for compound or electrochemical oxidation, is basically the ejection of electrons from the valence band, inciting the presence of compelling costs on fundamental polymers. Electrons can in like manner be brought to the conduction band, causing a n-kind doping. P-kind doping is through method of method for and huge more noteworthy ordinary than n-kind on account that most extreme n-kind doped coordinating polymers aren't as steady withinside the air because of oxidation through method of method for O₂. [9]

Charge carriers might be outlined all through doping by means of method of method for a redox response or protonation. The improvement of a polaron impacts from nearby bending of the primary polymer shape, followed through method of method for removal of an electron. Expecting some other electron is additionally disposed of from the valence band, a bipolar on might be delivered. For trans-polyacetylene, reciprocals exist, (i.e., degenerate, ground-realm structures), that vary basically withinside the shift of

twofold and unmarried securities. Thusly, while a bipolar on shape is created, they can straightforwardly separate (called a soliton). [10]

2.4. Synthesis of conducting polymers.

➤ Chemical

In an exhausting counterfeit polymerization, a monomer, a dopant, and an oxidant are harmed up in an answer saved at a chose temperature. The polymerization thing keeps on being problematic. Numerous investigation packs have taken at the cation-present day instrument even yet there's battle around the way connected with chain development.

➤ Electrochemical

Like counterfeit polymerization, the extreme cation is made at the primary develop thru a achieved restrict. In a normal electrochemical roadway, a restrict is done at some point of an electrolyte association containing a monomer and a dopant. A three-cathode (working, reference, counter cathodes) or a two-terminal (working, reference anodes) mode is in all likelihood used. Electrochemical polymerization is worthwhile, because the polymer wants now no longer problem with to be apathetic and sanitized. As attempted above, in each polymerization cases, the hidden give a boost to is the development of the extreme cation, observed thru coupling reaction of slight cations. [11]

2.5. Classes of Conducting Polymers

➤ Polyaniline

Polyaniline (PANI) is one of the greatest broadly contemplated coordinating polymers coming about because of its unobtrusive cost, advantageous mix, and simple doping/deducing. Be that since it might, the totally oxidized and decreased territory of PANI isn't driving. Just while the nicely oxidized states (essentially the emeraldine structure) are doped, does PANI develop to be conductive PANI might be coordinated artificially or on the other hand electrochemically. [12]

➤ Polythiophene

Polythiophene (PT) is one of the earliest notions approximately coordinating polymers with a low band opening (i.e., 2eV for un-substituted PT). Like PANI, PT is probably coordinated with the manual of a compound or besides electrochemical course. [13]

3. Effect Of Doping on the Properties of Carbon-Based Nano-Materials

The chamber homes are changed through the blend of hetero-particles unequivocally into a CNT. Subsequently, this limit of nitrogen atom substitute grades closer to the impact of pentagons and heptagons and broadens the reactivity of the connecting carbon particles, continuing in an unrivaled period of issue withinside the N-CNT while conversely, with a "pure" CNT. Doping changes the high-level development of CNTs through charge development. Since the band empty of the CNT is diminished to shape the metal CNTs with an over the top reactant movement, this influence has an effect at the

optoelectronic homes of the SWCNTs. The N-CNTs' pyridine-like N plans are viewed as responsible for their metal way of behaving and show separated features near the Fermi stage.

These electron-rich plans work n-kind nanotubes and capacity substantial styles for nuclear heterojunction gadgets. The CNT has unquestionable components depending at the sorts and wellsprings of the N sensible parties. Anyway, the hydrophilic man or woman of CNTs is through all commitments dope-subordinate, which will augment in light of the fact that the N content material risings. The water dispersibility of N-CNTs over diethylenetriamine was shown to be better than that of N-CNTs over hydrazine hydrate, which has more visible N particles (having significantly less N molecules). The N-doping CNTs' unnecessary hydrophilicity makes it harder for the electrolyte to stick to the CNTs, so they can't do their natural and helpful. [14]

The N-CNT has a lot bigger surface region than CNTs, subsequently biomolecules immobilize on them utilizing the standard genuine adsorption strategy. In any case, It is likewise realized that a cluttered collaboration between a protein and its surface can denature the protein. It was found that Goliath biomolecules, including proteins, are associated with the external layer of a chamber doped with unshared van der Waals energy bonds and seem to go through no conformational change during immobilization. Contrasted with their accomplice, MWCNTs, N-doped MWCNTs keep up with the right affirmation of metalloproteins, paying little heed to measure, charge, or subject of rot. The high surface adsorption limit and low nitrogen content advance electron move among dihydroxy benzene and the anode surface. Except for the superior blood and cell similarity of spiked MWCNTs, this element is non-harmful in vivo and in vitro. Electrochemical information likewise shows that the CN_x cathode with the most minimal nitrogen content \ (1 particle percent \) has the most noteworthy reversible constraint of 270mAhg⁻¹ with a ceaseless thickness of 0.2mAcm² and the most noteworthy business current thickness esteem.

Rather than the C particle in the NCNT structure, the higher the nitrogen content from two sources, N like pyridine and N like graphite, the higher the electron thickness in the external layer of the CN_x nanotube. When treated with corrosives, the additional electrons in CN_xNT show negative powerful positions, further developing the adsorption limit of the chamber. In spite of normal conviction, Thirimanne et al. The expanded development isn't relative to the aggregate sum of nitrogen and acknowledges that quaternary nitrogen (one more method of N expansion) likewise assumes a part in the upgraded impact of dissolvable tissue. NCNTs acquired at high temperatures of 80 ° C utilizing soluble base have the most noteworthy grouping of quaternary gathering. In any case, NCNTs with the most minimal nitrogen content at the superficial show better motor stream and cathode catalysis than undoped CNTs. Contrasted with sans-n-CNT beats, nitrogen hardening fundamentally affected the unwavering quality and selectivity of C = C security hydrogenation, bringing about a huge improvement in hydrogenation. [15]

4. Experimental

4.1. Method

Phenylenediamine (OPD) (ADWIC, Egypt), Potassium dichromate (Merck, Germany), Hydrochloric destructive damaging (32%), Sulfuric destructive horrendous (98%) Formic destructive disastrous (pretty much 100 percent). All of the corrosive substances used are (Merck, Germany). For filtering and UV visible estimates, CH_3CO and dimethyl sulfoxide (DMSO) are used separately. All synthetic materials, acids, and solvents were used in this experiment. as gotten minus any additional refinement.

4.2. Measurements

The FTIR spectra had been obtained the use of KBr pellet strategies on an FTIR 8201PC (Shimadzu) equipment. A spectrophotometer (UV1601 Shimadzu) changed into applied to gauge the UV considerable admission spectra. Warm exams had been completed in an surroundings of nitrogen making use of a Mettler Toledo 851 thermo gravimetric examination (TGA) from room temperature to 600 °C at a tempo of 10 °C/min. In the TGA take a look at, 15 mg of take a look at changed into located right into a platinum cauldron. At room temperature, conductivity estimations had been concerned with a conductivity meter. (CM30V).

4.3. Combination of poly(o-phenylenediamine) doped in various acids

1.622 g of phenylenediamine is separated in 100 mL of 0.1 M HCl in a chilled connected ice shower to spread out a homogenous plan. Before giving the key response 50 mL of 0.1 M HCl and combining for 30 minutes, potassium dichromate (4.413 g) was crushed. After spending 24 hours at room temperature, the association is filtered, washed with CH_3CO and plain water, and the polymer is dried for 24 hours in a reach at 60 °C. In the aforementioned framework destructive, 0.1 M H_2SO_4 , 0.1 M HCOOH , 0.1 M CH_3COOH , and 0.1 M H_3PO_4 were used individually.

5. Result and Discussion

5.1. Fourier change infrared spectroscopy (FTIR)

The significance of FTIR in our paintings is collected withinside the exam of band region for figuring out groupings existent withinside the doped poly phenylenediamine. The FTIR variety of PoPD doped in diverse acids is proven in Figure 2. It shows an enlargement withinside the variety of 32353432 cm^{-1} that is basically assigned to the polymer's vital and optionally available amino corporations. $\text{C}=\text{C}$ extending vibrations of the phenazine kind systems withinside the PoPD backbone may be attributed to the band withinside the variety 1602-1640 cm^{-1} . The quinoid and benzoic jewelry' CN extending vibrations seem withinside the degrees 14991502 cm^{-1} and 13571397 cm^{-1} , respectively.

The out of aircraft twisting motion of the CH responsibilities of the tetra subbed benzene cores of phenazine devices is projected to purpose the tops withinside the attain 834842 cm^{-1} . The lifestyles of corporations among 900 and 1040 cm^{-1} shows the prevalence of open jewelry within side the phenazine devices because of in plane twisting motion of the CH necessities of the 1,2,4trisubstituted benzene jewelry. Ring twisting is assigned to the signal within side the variety 512543 cm^{-1} . The FTIR spectrum for the alloying elements employed gets equivalent, indicating that the different dopants' oxidation degrees are close together.

The stabilizing tension is determined by the technique of method for components such as polymer circular pattern size, wildlife polymers content and composition plastic doping, etc. Figure 2.D demonstrates that a narrow strength band at 1397 cm^{-1} exists in the PoPD CH_3COOH spectrum. This is because the CN band has grown, while the ranges of PoPD H_2SO_4 and PoPD H_3PO_4 have strong strength bands at 1361 cm^{-1} and 1359 cm^{-1} , respectively. This shift to diminish wave reach might be ascribed to the decent doping levels of PoPD H_2SO_4 and PoPD H_3PO_4 , which favor electron advancement and prompt the migration to bring down wave number. [16]

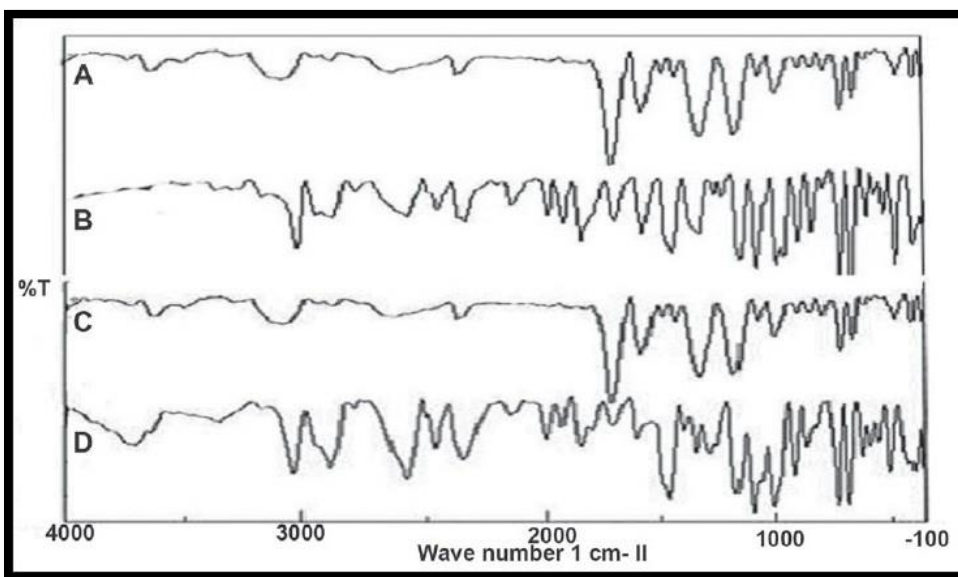


Figure 2: FTIR spectra of PoPD doped with (A) HCl, (B) H_2SO_4 , (C) HCOOH , (D) CH_3COOH

5.2. UV Visible spectroscopy

Figure 3 shows the UV Visible Spectrum of PoPD combined with a few dopants (HCl , H_2SO_4 , HCOOH , CH_3COOH , and H_3PO_4). Two trademark take-up tops were found in the 282429 nm range. The benzene * electron change is assigned a peak of 294 nm, and the n^* electron advance is assigned a peak of 429 nm. The blue shift from 294 nm to 282 nm may indicate a successful H_3PO_4 doping due to H_3PO_4 doped PoPD, which results in lower formation levels, impeded charge transfer between chains in PoPD. [17]

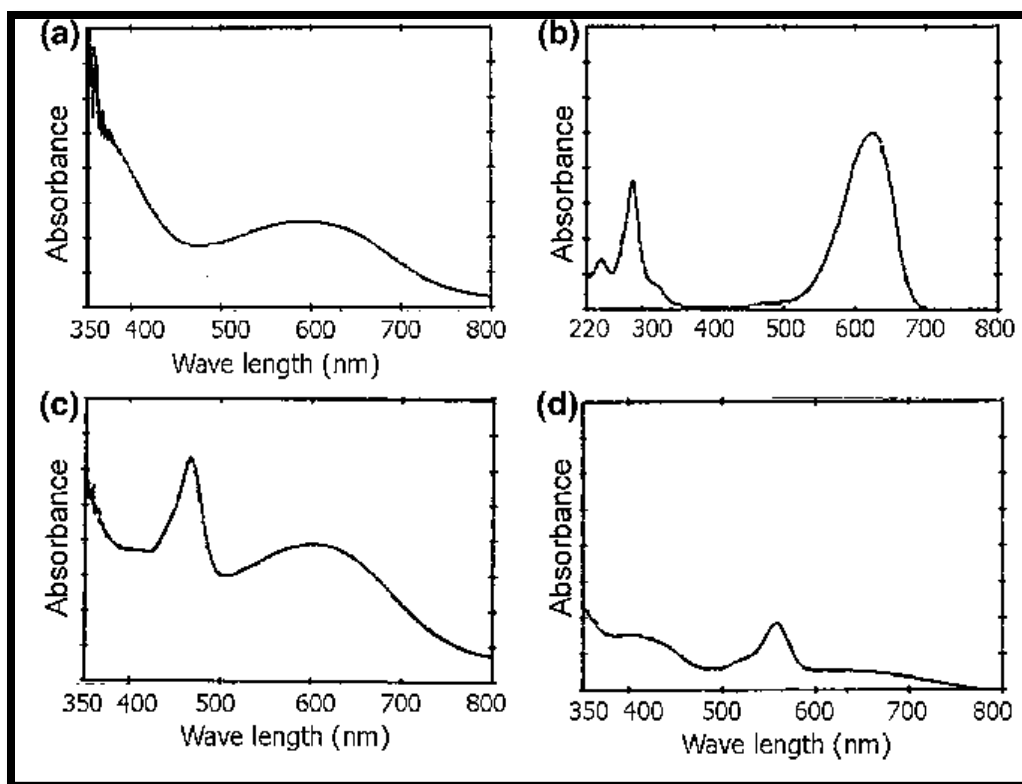


Figure 3: PoPD UVVis spectra doped with (A) HCl, (B) H₂SO₄, (C) HCOOH, and (D) CH₃COOH

5.3. Electrical conductivity

Table 1 shows the electrical conductivity of PoPDHCl, PoPDH₂SO₄, PoPDHCOOH, PoPDCH₃COOH, and PoPDH₃PO₄ at ambient temperature. The conductivity was calculated using the formula $\text{PoPDH}_2\text{SO}_4 = \text{PoPDH}_3\text{PO}_4 > \text{PoPDHCl} > \text{PoPDHCOOH} > \text{PoPDCH}_3\text{COOH}$ (Table 1). When CH₃COOH is used as a dopant for PoPD, the effectiveness of cost transfer between both the polymer chains is reduced, which leads to a decrease in conductivity value. In any event, PoPDH₂SO₄ and PoPDH₃PO₄ have the best electric conductivity advantages, demonstrating the incredible doping level of PoPD blasted with those acids. Figure 4 depicts how temperature affects the conductivity of PoPD made with certain alloying elements. It is apparent that when the temperature rose, the conductivity of the different corrosive dopants increased, which is characteristic of warmly actuated activity and is consistent with handwriting. The rise in conductance is believed to be the cause of highlighted. Moreover, atomic oscillation frequently ceases to be significant at high temperatures, leading to the mobility of perovskite nanoparticles and reconstituted particles. [18]

Table: 1. At room temperature, the electrical conductivity of PoPD in various acids dopants.

Polymer	Conductivity (S.cm ⁻¹)
HCl	2.36
H ₂ SO ₄	1.05

HCOOH	1.15
CH ₃ COOH	0.63

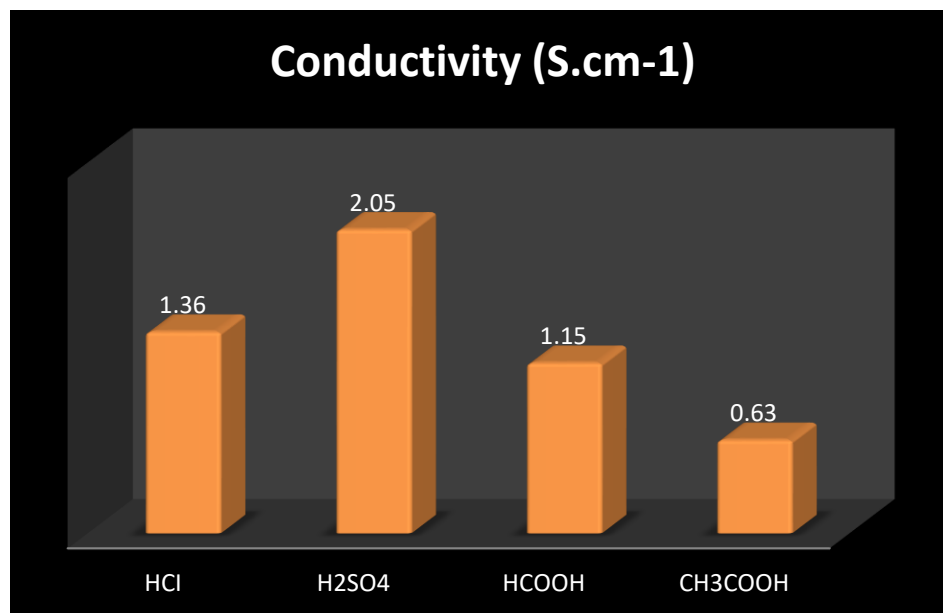


Figure: 4 conductivity plots of PoPD doped in various acids (A) HCl, (B) H₂SO₄, (C) HCOOH, and (D) CH₃COOH.

6. Conclusion

Most notable are the benefits in electrical properties from of doped with H₂SO₄ and H₃PO₄, which show that these acids are excellent for PoPD doping. The FTIR and UV Visible spectra both verify this truth. PoPD H₃PO₄ causes the dopant shortage to expand and while other dopants cause it to decrease. This may be the result of PoPDH₃PO₄ losing more charge than PoPD of other acids, which suggests that the degree of PoPD doping by H₃PO₄ is the greatest. CNT-N became added withinside the reaction of substance fume testimony withinside the sight of ethylene stream. [19] Here, peeled graphitic carbon nitride functionalized with nickel oxides has been applied as a starting cloth in CNT-N improvement. This cloth assumes a twofold component: (1) nickel became an impetus in nano-tube improvement and (2) graphitic carbon nitride stuffed in as assist for nickel nano-debris and as carbon/nitrogen source. The effects likewise reveal that ethylene assumes a crucial component withinside the improvement of cylinders. On one side, it carbon decreased the nickel oxide (II) to steel nickel which became a functioning degree withinside the improvement of the nanotubes, and, then again, it became a wellspring of carbon withinside the remaining example. [20] The N-doped nanotubes may display promising execution in exceptional packages like catalysis, lithium-particle batteries, exceptional capacitors, etc.

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