CHAPTER V

POLYPYRROLE AND POLYANILINE

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COUNTER ELECTRODES

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In the context of solar cells, counter electrodes are an integral component of certain types of devices, such as dye-sensitized solar cells (DSSCs) and some variations of perovskite solar cells. The main purpose of a counter electrode is to facilitate the regeneration of the redox couple involved in the photo conversion process.

In DSSCs, for example, the counter electrode typically consists of a conductive substrate (e.g., transparent conducting oxide) coated with a catalyst, often platinum or a platinum-based material. This electrode is placed opposite to the photoactive electrode (the working electrode) within the cell. The working electrode is generally an ITO or polymer layer and the counter electrode can be platinum, fullerene, graphene or polymer layer.

When light strikes the working electrode, it generates electron-hole pairs, initiating a photochemical reaction. The electrons flow through an external circuit, creating an electric current that can be harnessed. Meanwhile, the holes are consumed in a redox reaction with a liquid electrolyte and a dye molecule in the cell. To complete the circuit and enable a continuous flow of electrons, a counter electrode is used.

THE COUNTER ELECTRODE SERVES TWO ESSENTIAL FUNCTIONS:

1. Electron transfer: Once the holes are consumed in the redox reaction, a reduction process occurs at the counter electrode. The counter electrode catalyzes the reduction of the oxidized species in the electrolyte, effectively regenerating the redox couple. This process allows for the continuous cycling of the redox couple, enabling sustained current generation.

2. Charge balance: As electrons flow through the external circuit, a charge imbalance is created within the cell. The counter electrode provides a pathway for the flow of positive charge (ions) from the electrolyte to the working electrode, balancing the charge and maintaining electrical neutrality.

In solar cells, different types of counter electrodes are employed depending on the specific type of solar cell technology being used. Here are some commonly used counter electrode materials.

I. PLATINUM (PT): Platinum is a widely used counter electrode material due to its excellent catalytic properties for redox reactions. It is commonly used in dye-sensitized solar cells (DSSCs) and some variations of perovskite solar cells. Pt counter electrodes provide efficient regeneration of the redox couple and enable high-performance solar cell devices. However, platinum is expensive, which can limit its widespread adoption.

II. PLATINUM-BASED ALLOYS: To address the cost issue associated with pure platinum, researchers have explored platinum-based alloys as alternatives. For example, platinum-nickel (Pt-Ni) and platinum-cobalt (Pt-Co) alloys have been investigated for their catalytic properties and lower cost compared to pure platinum. These alloys can offer comparable or improved performance while reducing material costs.

III. CARBON-BASED MATERIALS: Carbon-based materials, such as graphite, carbon nanotubes and graphene can serve as effective counter electrodes in certain types of solar cells. These materials exhibit good electrical conductivity and can provide catalytic activity for redox reactions. Carbon-based counter electrodes are relatively low-cost and compatible with large-scale manufacturing processes.

IV. CONDUCTIVE POLYMERS: Conductive polymers, such as polyaniline and polypyrrole, have been explored as counter electrode materials. These polymers possess good electrical conductivity and can provide catalytic properties for redox reactions. Conductive polymers offer the advantage of being lightweight, flexible, and potentially more cost-effective than traditional metal-based counter electrodes.

Several conductive polymers have been investigated and used as counter electrodes in solar cells. Some commonly used polymer electrodes are:

a. Polyaniline (PANI): Polyaniline is a conducting polymer that exhibits high electrical conductivity and good catalytic activity. It can be synthesized in different forms, such as emeraldine base, emeraldine salt, or pernigraniline. PANI-based counter electrodes have been employed in DSSCs and organic solar cells. PANI facilitates redox reactions, effectively regenerating the redox couple in the cell.

b. Polypyrrole (PPy): Polypyrrole is another widely investigated conductive polymer used as a counter electrode. It possesses good electrical conductivity and can provide efficient catalysis for redox reactions. PPy-based counter electrodes have been employed in DSSCs and other types of solar cells. PPy facilitates the reduction reaction, enabling the regeneration of the redox couple.

c. Poly(3,4-ethylenedioxythiophene) (PEDOT): PEDOT is a conductive polymer known for its high electrical conductivity, transparency, and stability. It has been utilized as a counter electrode material in DSSCs and organic solar cells. PEDOT counter electrodes also promote efficient charge transfer and redox reactions.

The advantages of using polymers as counter electrodes are:

- **Cost-effectiveness:** Conductive polymers are generally more cost-effective compared to traditional metal-based counter electrode materials, such as platinum.
- **Flexibility:** Conductive polymers are lightweight and flexible, making them suitable for flexible and portable solar cell applications.
- **Processability:** Conductive polymers can be easily processed and deposited onto substrates using various techniques, including solution-based methods, making them compatible with large-scale manufacturing processes.
- **Tunability:** Conductive polymers can be chemically modified and tuned to optimize their electrical conductivity, catalytic activity and stability.
- **Environmental sustainability:** Conductive polymers are often considered more environmentally friendly than metal-based materials, as they can be synthesized from renewable sources available in abundance.

  The limitations include potential degradation over time and lower stability compared to certain metal-based counter electrode materials. Attempts are being made to optimize the performance of conductive polymer-based counter electrodes in solar cells.

V. METAL OXIDES: Certain metal oxides, such as Ruthenium Dioxide (RuO_2) and Iridium Oxide (IrO_2), have been utilized as counter electrode materials in specific solar cell technologies. These metal oxides exhibit higher catalytic activity and stability, making them suitable for certain applications. However, their usage is typically limited to specialized solar cell designs.

It's important to note that the choice of counter electrode material depends on various factors, including the specific solar cell technology, performance requirements, cost considerations and availability of materials. Ongoing research and development in the field continue to explore new materials and combinations to improve the efficiency and cost-effectiveness of solar cell devices.

In the present study, Polypyrrole and Polyaniline was synthesized for using them as counter electrode materials.

Synthesis of polypyrrole

Pyrrole was synthesized using two methods:

Method 1(PP1)

The process can be divided into four key steps.

Step 1: Dissolving Sodium Dodecyl Sulphate in Water

The first step involves the dissolution of sodium dodecyl sulphate (SDS) in 100 ml of precooled water at 0°C. SDS is an anionic surfactant commonly used in various applications, including as a detergent in cleaning products. When SDS is dissolved in water, it forms micelles due to its amphiphilic nature. The hydrophilic head of SDS interacts with water molecules while the hydrophobic tail forms clusters to form micelles. This process helps to solubilize hydrophobic compounds like pyrrole.

Step 2: Addition of Pyrrole

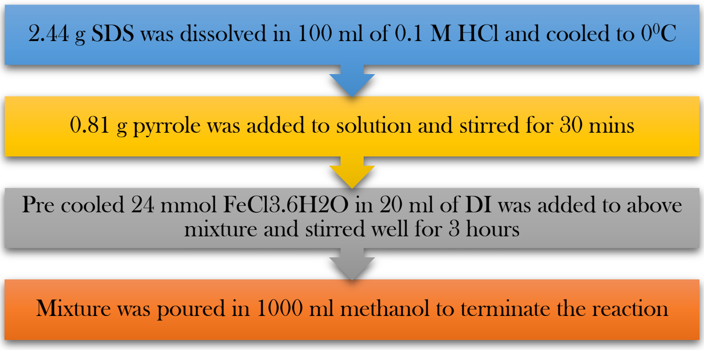
In the next step, 0.81 g of pyrrole is added to the SDS solution and the mixture is stirred for 30 minutes. Pyrrole is a five-membered heterocyclic compound that contains a nitrogen atom in the ring. It is insoluble in water, but the presence of SDS micelles helps to solubilize it in the solution. Stirring is necessary to ensure that the pyrrole is evenly dispersed throughout the solution.

Step 3: Addition of Ferric Chloride and Reaction

The third step involves the addition of ferric chloride, which acts as a Lewis acid catalyst, to the pyrrole/SDS solution. Ferric chloride is first dissolved in 20 ml of deionized water (DI) and added to the reaction mixture. The mixture is then allowed to react for 3 hours. During this time, ferric chloride promotes the cyclization of pyrrole to form a polymer. The SDS micelles solubilize the polymer in the solution.

Step 4: Termination and Formation of Ink

After the reaction is complete, it is terminated by adding the reaction mixture to 1000 ml methanol. This step stops the reaction from progressing any further. The resulting mixture is filtered, washed and dried to obtain a powder. This powder can be used to form an ink.



2.44 g SDS was dissolved in 100 ml of 0.1 M HCl and cooled to 0^0C

0.81 g pyrrole was added to solution and stirred for 30 mins

Pre cooled 24 mmol FeCl3.6H2O in 20 ml of DI was added to above mixture and stirred well for 3 hours

Mixture was poured in 1000 ml methanol to terminate the reaction

Figure 38: Flow chart for the synthesis of PPY1

METHOD 2 (PP2)

STEP 1: PREPARATION OF METHYL ORANGE SOLUTION

320 ml solution of 5 mM Methyl Orange was prepared by dissolving the required amount of Methyl Orange in distilled water and stirring until it was completely dissolved.

STEP 2: ADDITION OF $FECL_3.6H_2O$

2.592 grams of $FeCl_3.6H_2O$ was added to the Methyl Orange solution. The mixture was constantly stirred for 30 minutes to ensure complete dissolution of $FeCl_3$.

STEP 3: ADDITION OF PYRROLE

0.56 ml of pyrrole was added dropwise to the mixture while stirring at 0°C for 4 hours. The pyrrole molecules polymerized in the presence of $FeCl_3.6H_2O$ to form a polypyrrole material.

STEP 4: WASHING OF THE SAMPLE

The resulting sample was washed with DI water several times to remove any residual impurities and unreacted materials.

STEP 5: DOPING THE SAMPLE

The washed sample was kept in 2M HCl solution for 12 hours for doping of chlorine in the sample. This increases its conductivity and improves its electrical properties.

STEP 6: WASHING AND DRYING OF THE SAMPLE

The doped sample was washed again with distilled water to remove any residual HCl and then dried at room temperature.

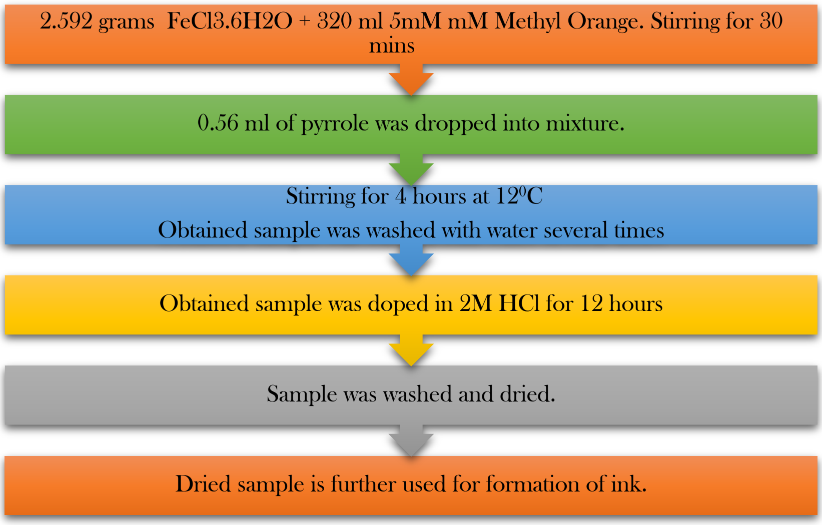


Figure 39: Flow chart for the synthesis of PPY2

The role of Methyl Orange in this synthesis process is to act as a surfactant, which helps to stabilize the polypyrrole particles during the synthesis process. Methyl Orange is a water-soluble dye that has both hydrophobic and hydrophilic properties. The hydrophobic part of the molecule interacts with the hydrophobic polypyrrole particles, while the hydrophilic part interacts with the water molecules in the solution. This interaction helps to prevent the aggregation of polypyrrole particles and promotes their uniform dispersion in the solution, leading to the formation of a high-quality polypyrrole material.

Methyl Orange controls the size and morphology of the resulting polymer particles also. The surfactant properties of Methyl Orange allow it to interact with the growing polypyrrole particles in the solution, thereby stabilizing them. This results in the formation of small and uniform polypyrrole particles.

The size of the polypyrrole particles is largely determined by the concentration of Methyl Orange in the solution. Higher concentrations of Methyl Orange lead to smaller particle sizes, as the surfactant molecules are more effective in stabilizing the growing particles. On the other hand, lower concentrations of Methyl Orange result in larger particle sizes, as the surfactant molecules are less effective in preventing particle aggregation.

In addition to controlling the size of the polypyrrole particles, Methyl Orange can also influence their morphology. By adjusting the concentration of Methyl Orange, it is possible to control the branching and shape of the polypyrrole particles. This is because the surfactant molecules can selectively interact with different phases of the growing particles, leading to the formation of different morphologies.

Overall, the role of Methyl Orange in modulating the size and morphology of polypyrrole particles is important in the synthesis of high-quality polypyrrole materials with tailored properties for various applications.

SYNTHESIS OF POLYANILINE

Polyaniline was synthesized using two methods:

METHOD 1 (PA1)

STEP 1:

A solution was prepared by mixing 1.5 ml of aniline and 50 ml of 1 M H_2SO_4. While aniline is an organic compound containing an amino group H_2SO_4 is a strong acid commonly used as a catalyst in organic reactions.

STEP 2:

The mixture was cooled to a temperature of 5°C and allowed to react for 30 mins.

STEP 3:

After the completion of initial reaction, 50 ml of 0.125 M APS (Ammonium Persulfate) was added to the reaction mixture. APS is a commonly used oxidizing agent that can be used to initiate polymerization reactions.

STEP 4:

The reaction mixture was then stirred vigorously for a period of 12 hours. During this time, the APS initiates a polymerization reaction involving the aniline.

STEP 5:

After the reaction was complete, the resulting product was washed and dried. This step involved the use of solvents and other washing agents to remove any remaining impurities from the product.

STEP 6:

The dried sample was then used for the formation of ink.

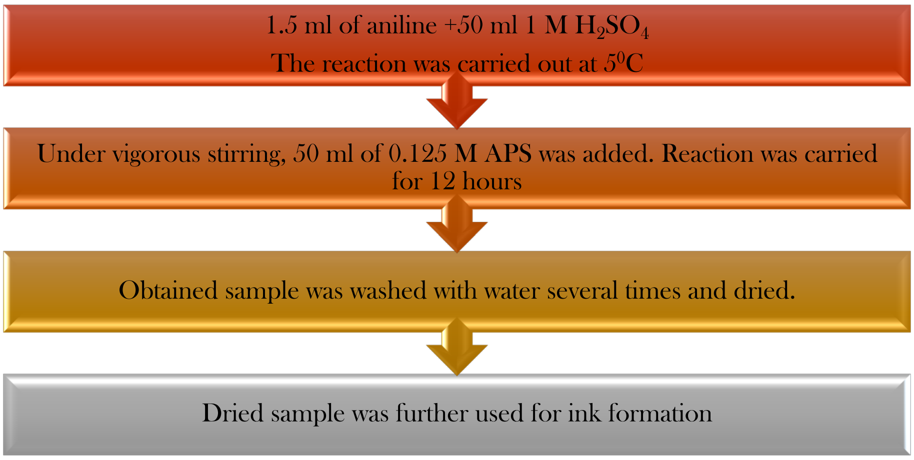


Figure 40: Flow chart for the synthesis of PA1

Method 2 (PA2)

Step 1:

To a solution of 16 mmol of aniline in 50 ml of 0.8 M hydrochloric acid (HCl), 4 mmol of ammonium persulfate (APS) was added.

Step 2:

The mixture was then placed in an ultrasonic bath for 90 seconds to ensure proper mixing and dispersion of the reactants.

Step 3:

The reaction mixture was then kept for 12 hours at a temperature of 4°C. During this time, the aniline monomers polymerized to form PANI nano fibers.

Step 4:

The resulting PANI nano fibers were then filtered and washed with deionized water several times to remove any residual solvent or impurities.

Step 5:

The washed fibers were allowed to dry completely before being used for the formation of ink.

Overall, the process involves the oxidative polymerization of aniline with APS as the oxidizing agent in acidic conditions. The ultrasonic bath was used to enhance the mixing and dispersion of the reactants, while the prolonged reaction time and elevated temperature were necessary for the formation of PANI nano fibers.

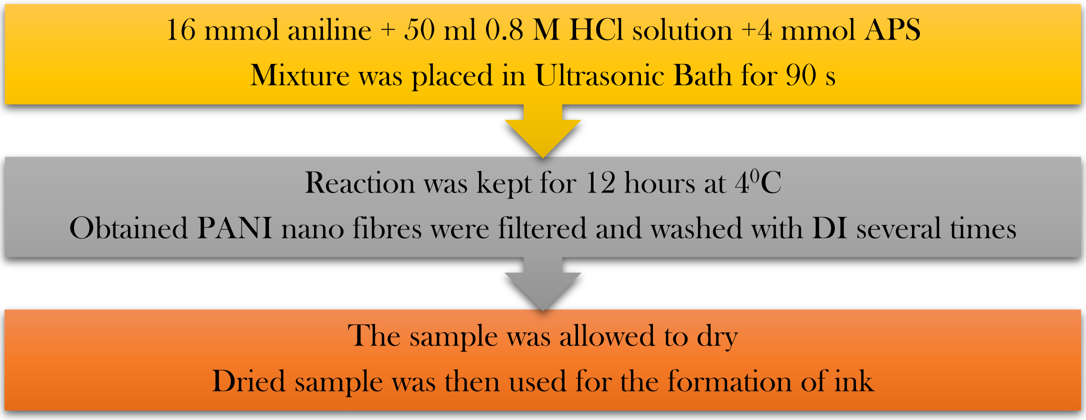


Figure 41: Flow chart for the synthesis of PA2

The process of coating a polymer powder onto a device is an important step in the development of various electronic devices, especially in the field of organic electronics. This process involves the dispersion of the polymer powder in a suitable solvent to create a polymer solution, which is then coated onto the device. The coated polymer must have good adhesive properties to ensure that the configuration of the device remains intact even when it is dipped into LHCs for its absorption. Additionally, the polymer dispersion must dry at room temperature, as the cells are formulated in substrates of moderate thermal stability. Finally, the formulated dispersion must not change the properties of the polymer majorly, particularly its conductivity.

To achieve the appropriate consistency of the polymer dispersion, it is necessary to carefully select the solvent used to dissolve the polymer powder (Hwang et al. 2008). The solvent should be able to dissolve the polymer completely, while also allowing for easy coating and drying at room temperature. Solvents such as chloroform and tetrahydrofuran (THF) are commonly used for this purpose, as they have good solubility for many organic polymers and can be easily evaporated at room temperature (Prévoteau et al. 2012).

The adhesive properties of the coated polymer are critical for the successful integration of the device. The adhesion between the polymer and the substrate is determined by the surface energy of both materials. In general, the adhesion is better when the surface energies of the two materials are similar. Therefore, it is important to choose a polymer that has a similar surface energy to that of the substrate. Additionally, the surface of the substrate can be modified to enhance the adhesion. For example, plasma treatment or the use of adhesion promoters can increase the surface energy of the substrate, leading to better adhesion (Cheng & Grest 2016).

The drying of the coated polymer at room temperature is an important consideration, especially for substrates of moderate thermal stability. Drying the coated polymer by heating could lead to thermal degradation of the substrate, which can affect the performance of the device. Therefore, it is essential to select a polymer that can be dried at room temperature. The drying process can be accelerated by increasing the air flow or reducing the humidity of the environment. Additionally, the use of additives such as surfactants or viscosity modifiers can improve the drying properties of the polymer dispersion (Jakubka et al. 2012).

Finally, it is crucial to maintain the conductivity of the polymer during the formulation process. Conductivity is a critical property for many electronic devices and any changes in conductivity can affect the performance of the device. The conductivity of the polymer can be affected by many factors, including the choice of solvent, the drying conditions and the presence of impurities. Therefore, it is important to carefully control these factors during the formulation process to ensure that the conductivity of the polymer is not significantly altered (Kang & Taton 2003).

In conclusion, the formulation of a polymer dispersion for coating onto a device requires careful consideration of many factors, including solvent selection, adhesion, drying conditions, and conductivity. The appropriate selection of these factors is critical for the successful integration of the device and the maintenance of its performance.

The ink is a mixture of the polymer powder and solvents isopropyl alcohol and Terpineol with ethyl cellulose as binder. Ethyl cellulose is a common polymer that is used in various applications due to its excellent film-forming properties. It is a derivative of cellulose and is soluble in many organic solvents, including isopropyl alcohol. In the ink formulation, ethyl cellulose acts as a binder between the polymer and Terpineol. The use of ethyl cellulose in the ink formulation ensures that the coated polymer adheres well to the substrate, leading to a stable device configuration. The amount of ethyl cellulose used in the ink formulation must be carefully controlled to avoid any negative effects on the conductivity of the polymer. Excessive amounts of ethyl cellulose can lead to a decrease in conductivity, while insufficient amounts can result in poor adhesion between the polymer and the substrate.

Terpineol is a terpene alcohol that is commonly used as a solvent in ink formulations (Jouault et al. 2014). It is a clear liquid with a pleasant odour and is soluble in many organic solvents. In the ink composition, Terpineol plays a critical role in maintaining the viscosity of the polymer solution. It acts as a plasticizer, which reduces the viscosity of the polymer solution and improves its flow properties. Terpineol also helps to ensure proper adhesion between the polymer and the substrate. The amount of Terpineol used in the ink formulation must be carefully controlled to avoid any negative effects on the drying of the coated polymer. Insufficient amounts of Terpineol can lead to poor adhesion, while excessive amounts can result in improper drying of the coated polymer at room temperature.

Isopropyl alcohol is a common organic solvent that is used to dissolve ethyl cellulose and the polymer powder (Bayarkhuu et al. 2020). It is a colorless, flammable liquid with a strong odour having excellent solvency properties and is commonly used in the formulation of inks and coatings. It is used in the ink composition to dissolve the polymer powder and ethyl cellulose and to ensure a homogeneous mixture of all the components.

The polymer powder used in the ink composition determines the conductivity and other physical properties of the coated polymer. The choice of polymer powder depends on the specific application and the desired properties of the device. In the ink formulation, the polymer powder is dissolved in the isopropyl alcohol with the help of ethyl cellulose and Terpineol. The amount of polymer powder used in the ink formulation must be carefully controlled to ensure proper conductivity and adhesion between the polymer and the substrate.

Ink Formulation:

Step 1: Dissolving of ethyl cellulose in isopropyl alcohol

Desired amount of ethyl cellulose is measured and taken into a container in which iso propyl alcohol is added. Mixture is stirred vigorously until the ethyl cellulose is completely dissolved.

Step 2: Mixing of polymer with the ethyl cellulose solution

Required amount of polymer is measured and added to the ethyl cellulose solution, till a sticky paste is obtained.

Step 3: Adding of Terpineol to the mixture

Measured amount of Terpineol is added to above mixture and stirred till the teripeol is fully incorporated.

Step 4: Packaging of the ink

The ink is transferred to a suitable container, labeled and suitably stored.

Composition of Ink

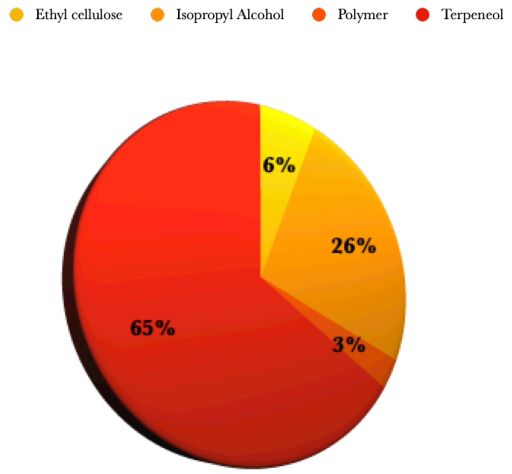


Figure 42: Percentage composition of ink

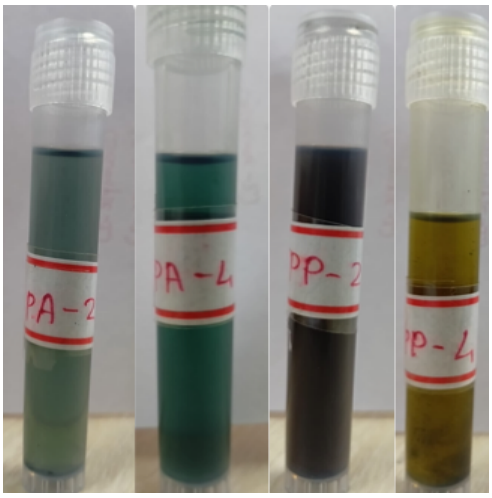


Figure 43: Final Inks

1.1. XRD and Particle size analysis of polymers

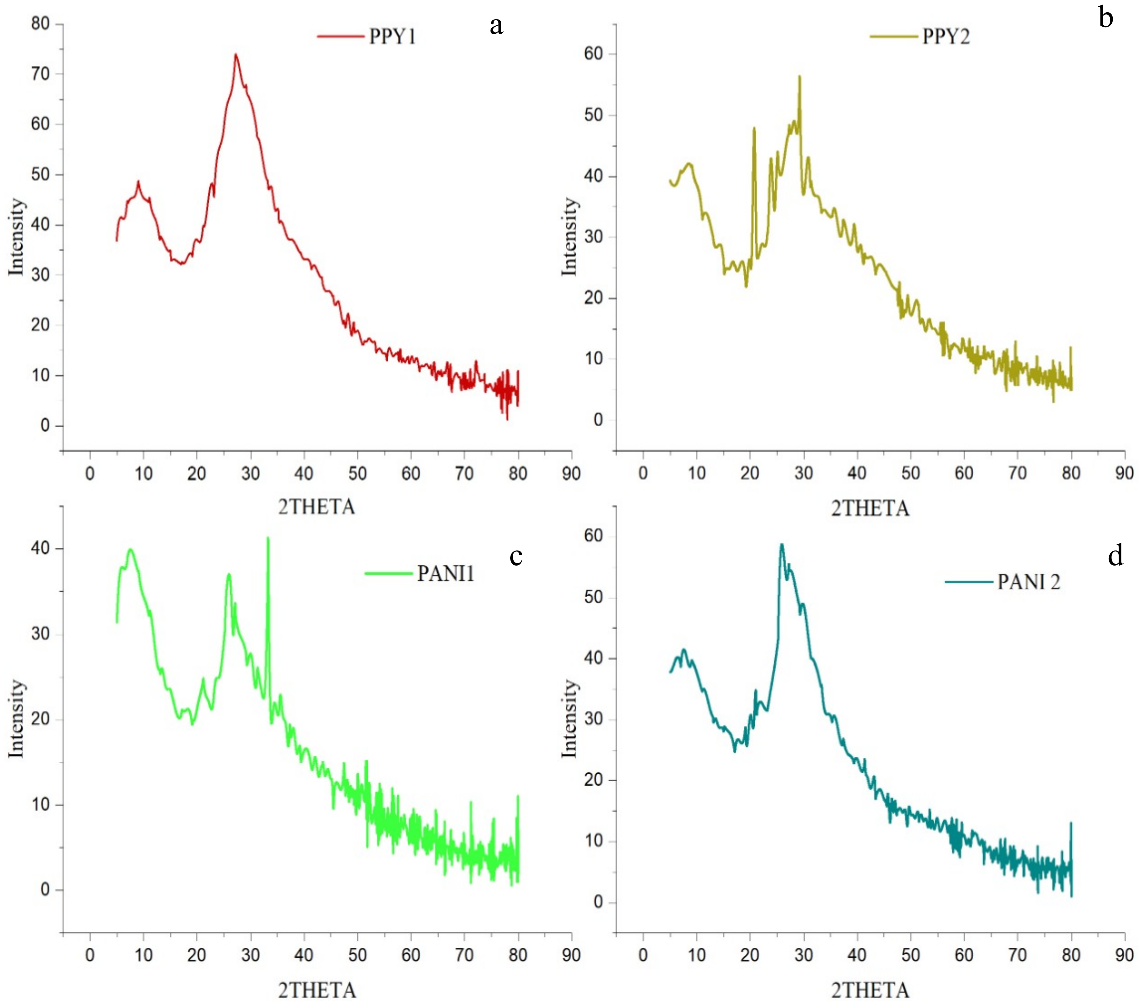


Figure 44: XRD Analysis of Polymers

After the synthesis of polypyrrole and polyaniline using chemical oxidative polymerization, X-ray diffraction (XRD) analysis was employed to characterize the resulting polymers. The XRD analysis revealed major peaks for polypyrrole at a 2θ value of 29°, which corresponds to the literature-reported peaks for polypyrrole. Similarly, for polyaniline, the XRD analysis showed peaks at 2θ value of 25°, which are consistent with the characteristic peaks of polyaniline. Additionally, the XRD patterns indicated broad peaks, confirming the amorphous nature of the synthesized polymers. (Leonavicius et al. 2011, Shukla et al. 2022, Agrawal et al. 2020, Liang et al. 2017)

1.2. UV-VIS CHARACTERISTICS OF POLYMERS

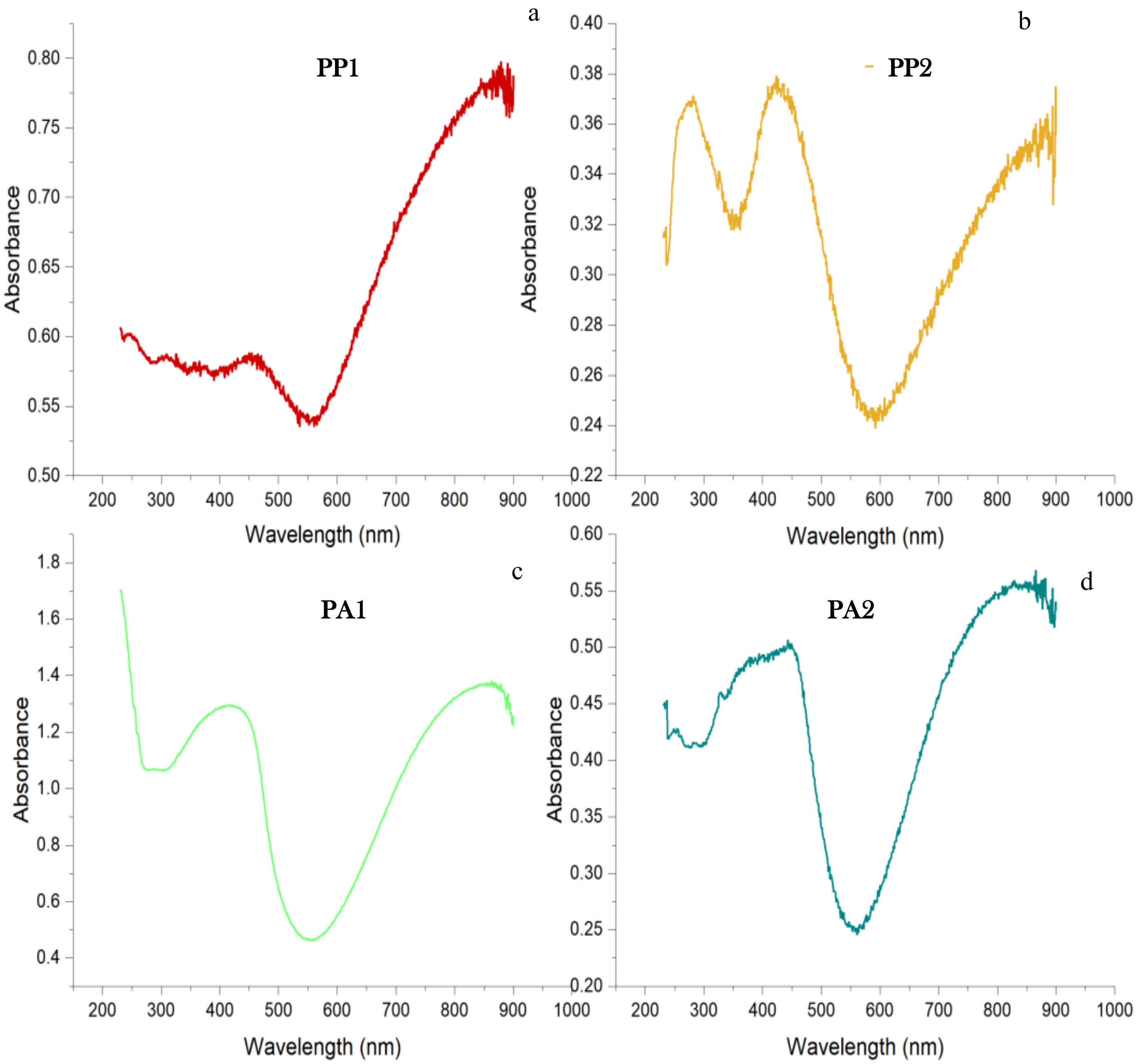


Figure 45: UV-Vis Absorbance Spectra of Polymers

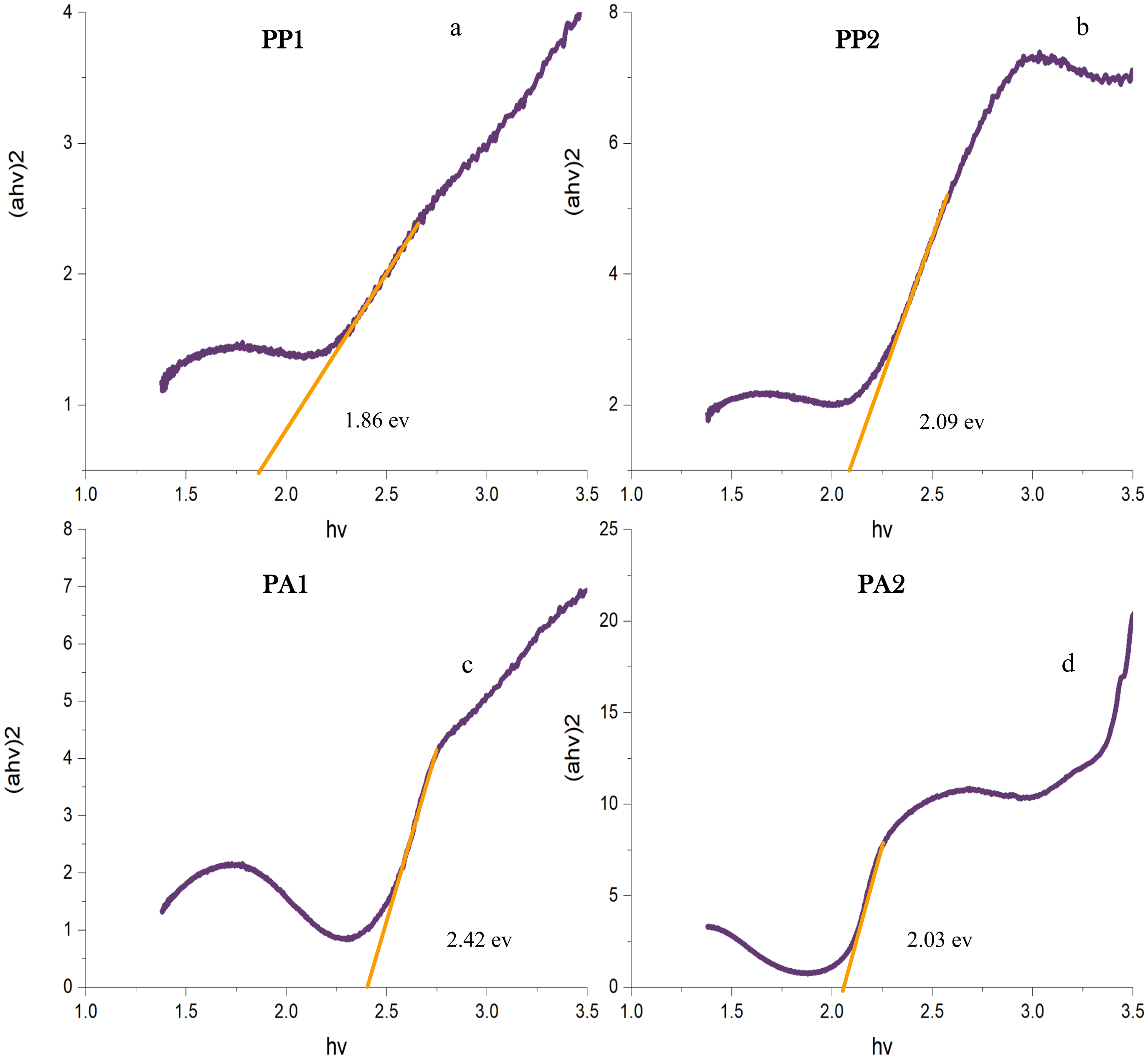


Figure 46: Tauc's Plot

UV-Vis analysis of polymers was performed to calculate the band gap of the materials. For both samples of polypyrrole, the major peak was obtained at around 430 nm which is the characteristic peak of polypyrrole and is in agreement with the literature. However, the Tauc's plot gave the values of band gap at 1.86 eV for PP1 and 2.09 eV for PP2. It must be noted that another peak at 250 nm was observed for PP2 which corresponds to methyl orange. For polyaniline the absorbance peaks were obtained at around 390 nm corresponding to its characteristic value of absorbance. The band gap values are 2.42 ev and 2.03 ev respectively for samples PA1 and PA2. These lower values of band gap would allow the polymers to serve as good counter electrodes. (Rheinstädter et al. 2014, Suhailath et al. 2016, Boddula & Palaniappan 2015, Yoshimoto et al. 2004)