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## Synthesis and characterization of organic poly (3, 4-ethylene dioxythiophene)-polystyrene sulfonate (PEDOT: PSS) and study of its electrical properties

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### Abstract

Conductive polymers (CPs), including poly (3, 4-ethylene dioxythiophene) (PEDOT): poly (styrene sulphonate) (PSS) in particular, have recently attracted a significant amount of interest from researchers for usage in bioelectronics applications. The in-situ polymerization technique was utilized to prepare the pure PEDOT: PSS that could be manufactured. In order to analyze the chemical structure and optical characteristics of the newly synthesized materials, several spectroscopic techniques such as X-ray diffractometry, UV-Vis spectrophotometer, Fourier transform infrared spectroscopy, and Raman spectroscopy was utilized. In addition, scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) were utilized to investigate the material's morphological characteristics. The article has studied the sample's electrical properties and other characteristics, and the applications of PEDOT: PSS in several areas have been discussed.

**Keywords:** Poly (3, 4-ethylene dioxythiophene): polystyrene sulfonate, PEDOT: PSS, electrical, synthesis

### Introduction

Conductive polymers (CPs), including poly (3, 4-ethylene dioxythiophene) (PEDOT): poly (styrene sulphonate) (PSS) in particular, have recently attracted a significant amount of interest from researchers for usage in the fabrication of functional applications. This can be ascribed to the great degree of adaptability and superior electrical conductivity of CPs. This investigation provided insight into the PSS mechanisms that give PEDOT its improved electrical conductivity. As a result, the main objective is to increase the electrical efficiency of doped PEDOT: PSS using novel techniques, including enduring treatment and secondary dopants. Additionally, it applies a rigorous approach to several key factors that significantly affect its conductivity. We illustrate the potential of dopant PEDOT: PSS over several intriguing applications in fields such as chemical sensors, energy storage, solar cell, and other usage through an in-depth assessment of the most recent studies conducted by different research groups over the past few years. These studies were carried out over the course of the past few years. Conductive polymers, also known as CPs, are well-known as advanced textiles that combine one-of-a-kind structural features, such as charge transfer as well as electro-optic properties. Typical polymers have great versatility in computation and are also very easy to synthesize [1-3]. This is due to their ability to deliver electrical, chemical, and electromagnetic impulses to the target area. The breakthrough that found evidence of conductive polymers came in 1977 with the high conductivity of polyacetylene-doped iodine as a p-type dopant. This led to the discovery of conductive polymers (oxidizing agents). In 1978, polyacetylene that had been combined with an n-type dopant (reduction agent) demonstrated a conductivity effect. These early studies on polyacetylene sparked an interest in using polymer electrolytes for finished applications due to their stimulating effects. It is interesting to note that PEDOT: PSS have good computer / electronic characteristics, and they also offer reasonable control of the electrical stimuli attributed to the prevalence of conjugate p-electrons in the spine of the molecule [4]. PEDOT: PSS is a conducting polymer that provides good clarity, density, inertness, high thermal conductivity, excellent adhesion, flexibility, and a cheap cost of manufacture using solution-dependent aqueous coating processes.

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This study aims to give an overview of PEDOT: PSS characteristics, calculate the complicated index of refraction of a PEDOT: PSS hybrid with oxidation process doping adjustment, and study the electrical properties with broad applications.

### **Theoretical overview of PEDOT: PSS characteristics Significance of the PEDOT: PSS**

Conducting polymers are a Nobel prize-winning organic substance with remarkable electro-optical characteristics mimicking ordinary inorganic semiconductors and elements. As a result, it has gained a great deal of interest. PEDOT: PSS is a polymer that is a blend of two polymer electrolytes called poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS). This combination contains sodium polystyrene sulfonate, which is a kind of sulfonated polystyrene. It is one of the components in this mixture. A portion of the sulfonyl groups has had their proton removed, resulting in a negative charge on those parts. The second component, known as poly (3,4-ethylene dioxythiophene) (PEDOT), is a conjugated polymer based on conducting polymers, transports positive charges, and is a chained polymeric. They charged molecules together using a molecular charging system. The synthesis of PEDOT: PSS may be performed utilizing straightforward, flexible, cost-effective, and easily adaptable methods [5, 6]. They exhibit the characteristic of self-assembled biomolecule structures while retaining high functioning en route through electrical techniques. Their coiled strands, as well as their polarizability and utilized the concept structures, make up quasiparticles that can be either singly or doubly charged. Carbon nanotubes (CNTs), emission nanowires (CNWs), graphene oxide (GO), and metallic atoms are already used as electrical conductors; however, the efficient and extensive use of these materials has been limited because they are not biodegradable, there is insufficient evidence regarding their toxicity *in vivo*, and reinforced systems contain conducting particles that are dispersed in an anisotropic manner [7, 8]. PEDOT, which is one of the primary and most successful electrode materials, has its application domain in a variety of domains, such as energy storage applications, biosensors, solar cells, detection, and rechargeable batteries. Its software spans various fields [9].

### **The mechanical characteristics of PEDOT: PSS**

Because PEDOT: PSS is most typically utilized in thin-film designs, various approaches for properly probing its mechanical characteristics have been developed. A water-supported strain gauge, four-point bend trials to evaluate good adhesion yield stress, buckling experiments to examine modulus, and bend tests on PDMS and HDPE support to investigate crack initiation strain are the approaches that have been utilized. Because PEDOT: PSS is the most often utilized material in thin-film structures, all of these approaches were created [10].

Even though PEDOT: PSS has poor electrical portability than silicon, which can also be incorporated into electronics via stress-relief structures, PEDOT: PSS is flexible and can edition processing, including roll-to-roll handling. Silicon, on the other hand, has higher electrical mobility than PEDOT: PSS and can be incorporated into wearable electronics via strain constructions. Silicon can also be integrated into flexible electronics via stress-relief

structures. When it comes to the use of organic semiconductors in thin-film constructions, the properties of having a low stiffness when the material is in the elastic region and a high degree of ductility immediately before breakage are considered to be the most relevant qualities. It has been observed that these features are significantly linked to relative humidity. When the relative humidity is high (above 40 percent), the PSS absorbs more water, weakening the material's hydrogen bonds. This causes the material to be able to stretch further before breaking and results in a lower elastic modulus. The fact that strong bonds remain between PSS grains even when the relative humidity is low (23 percent) causes the material to have a higher modulus and a lower strain before it fractures. It is believed that films with a higher relative humidity fail as a result of intergranular fracture, whereas films with a lower relative humidity fail as a result of the transgranular fracture. Even at low concentrations of 1 weight percent, additives like 3-glycidioxypropyltrimethoxysilane (GOPS) may considerably boost mechanical stability in aqueous systems without appreciably compromising electrical properties [11, 12].

Although it has lower electrical motility than silica, which may be integrated into flexible electronics by means of stress-relief devices, PEDOT: PSS can enable processes with reduced costs, like roll-to-roll sequencing, for example. These approaches can also be used to incorporate silicon into flexible electronics. The most crucial properties of semiconductors for usage in thin-film structures are a low modulus of elasticity and a high degree of stretchability immediately before fracture. These variables were discovered to have a strong relationship with relative humidity. Water is absorbed when the relative humidity is high (over 40%), and the PSS hydrogen bonds weaken. As a direct consequence of this, the PSS possesses a greater strain before fracture in addition to inferior moduli. Strong bonding between PSS grains in a low relative humidity environment results in higher modulus and reduced strain prior to fracture (23 percent). Films with a lower comparative humidity are more likely to fail through a process known as a trans-granular fracture, while films with a greater relative humidity are more likely to fail through the process known as inter-granular rupture. Additives such as loading rate (GOPS), even at levels as low as one percent by weight, are able to considerably increase mechanical integrity in alkaline solutions without changing the electrical properties of the system [13].

### **Electrical properties of PEDOT: PSS**

In this article, the authors offer an easy approach for optimizing the characteristics of poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT: PSS) films; as well as their application in heterostructure devices and polymer photovoltaic panels. Using this method improves the electrical properties of the movie and makes them easier to optimize. It is possible to enhance the performance of the PEDOT: PSS solution by using the organic solvents n-methyl-2-pyrrolidone and methanol, in addition to dimethyl sulfoxide. This is done to make combining the solvent effect more straightforward. The range of electrical conductivity, which can be anywhere from 0.16 to 194 S/cm, is very sensitive to the quantity of n-methyl-2-pyrrolidone in the solution. It has been demonstrated that the conductivity of PEDOT: PSS films

incorporating co-solvents may be boosted by three orders of magnitude in comparison to the conductivity of pure PEDOT: PSS. This is achieved while maintaining a level of transparency in the viewing zone that is greater than 92 percent <sup>[14]</sup>.

### Applications of the PEDOT: PSS

Because PEDOT: PSS has the maximum accuracy of any semiconducting absorber layer, it is suitable for application in pliable and recyclable teigs. Nevertheless, its principal application is as a polymer that possesses great ductility, transparency, and electrical conductivity. For example, AGFA coatings 200 million photographic films per year with a layer of nearly colorless and transparent material that has been extensively thinned down and stretched out. This material has been subjected to severe thinning and stretching. PSS is being used as an electrolyte in polymer electrochemical capacitors and as an occlusive additive to avoid electrical discharges during manufacture and normal film usage, regardless of humidity. Both these uses for PSS are important to the industry. The Physical Statics Society created PEDOT (PSS) <sup>[15]</sup>. The addition of organic substances, such as high-boiling solvents like methyl pyrrolidone, dimethyl sulfoxide, sorbitol, ionic liquids, and surfactants, increases the conductivity of the combination significantly. As a consequence of this, it is also appropriate for use as an electrocatalyst, such as in small screens, organic lamp diodes, [flexible organic solar cells, and electronic papers. In these applications, it can supersede indium titanium dioxide, the material of choice in the past (ITO) <sup>[16]</sup>. Because of its electrical purity, which may reach up to 4600 S/cm, it can be utilized as a current collector in capacitors rather than silicon dioxide or liquid electrolytes. In addition to that, it is a necessary component in the production of organic electrochemical transistors. The conductance of PEDOT can be considerably improved with the use of after-treatment applications of glycol, sodium thiosulfate (DMSO), salts, allision, eligible for the deduction, acids, isopropanol, phenol, vicinal diols, and hydrophilic polymers chloro. It is possible for the permeability of the tangible PEDOT: PSS, which is used in flexible organic devices, to be increased by a factor of 3 if a network of nanoparticles and gold nanowires is implanted into the substance. This would make the material competitive with ITO, which is a common translucent electrode substance <sup>[17]</sup>. When utilized as a gelled particle dispersion in water, PEDOT: PSS has extensive use. Spin coating is commonly used to apply a thin layer of dispersion to glass, and then heat is used to remove the water, leaving a conductive layer.

To accommodate a variety of coating and printing processes, specialized PEDOT: PSS inks and formulas were created. Printed circuit board (PCB) inks, flexography inks, rotogravure inks, and inkjet inks are all common applications for PEDOT-based PSS inks. For screen-printing techniques that need a highly viscous paste that dries slowly, PEDOT: PSS can also be provided in high boiling solvents like propanediol. This is a viable alternative when exact parameters are required. Pellets made of freeze-dried PEDOT: PSS can be dispersed in water and other solvents. For instance, this speeds up the drying time for prints made with ethanol. PEDOT: PSS UV-stabilizers are now available to counteract the deterioration caused by exposure to sunlight and extremes of heat and humidity <sup>[16]</sup>.

## Experimental

### Preparation of the PEDOT: PSS Materials

The synthesis of Baytron P was utilized to produce PEDOT: PSS samples with different amounts of the PSS component. 3 In this method, the monomer 3,4-ethylenedioxythiophene, which has a purity of 97 percent, is polymerized at room temperature in an aqueous solution of poly(4-styrenesulfonic acid), which has an average molecular weight of 14.7 million, with sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ , which has a purity of 99 percent) serving as the oxidizing agent. When poly (4-styrenesulfonic acid), oxygen, and an initiator are added to the less favorable monomer EDOT, we expect it to be entirely transformed into the more advantageous PEDOT <sup>[18]</sup>. As a consequence, solutions of PEDOT: PSS with various PEDOT-to-PSS ratios were created by varying the amount of aqueous EDOT and PSS solutions to accommodate for the educts' differing densities. These solutions were subsequently given meaningful names. The EDOT: PSS combination, when dissolved in deionized water at room temperature for ten minutes, produced aqueous solutions that contained 2.3 weight percent of the mixture. For ten minutes, 1 mol of  $\text{Na}_2\text{S}_2\text{O}_8$  was added to 2 mol of 3,4-ylenedioxythiophene while the mixture was agitated. After stirring for twenty-four hours, a dark blue dispersed PEDOT: PSS was generated after adding  $\text{Fe}_2(\text{SO}_4)_3$  to initiate the polymerization process. After that, the solution was filtered under vacuum using a filter that had a porosity of between 4 and 7 microns.

### Characterization

XRD diffraction patterns of PEDOT: PSS were obtained by utilizing a Brucker diffractometer (D8 Advance, Germany) in conjunction with a Cu K radiation source (= 1.54059) operating at a power setting of 1600 w (40 kV, 40 mA) in the 2theta range (50-650). In order to analyze the materials' absorption spectra, an IRAffinity-1S (Shimadzu, Japan) spectrophotometer was utilized to record FTIR spectra from a range of 4000  $\text{cm}^{-1}$  to 600  $\text{cm}^{-1}$  during the course of the experiment. The Raman spectra ranging from 200  $\text{cm}^{-1}$  to 3000  $\text{cm}^{-1}$  were obtained by employing a laser with a wavelength of 785 nm as the source of the excitation wavelength and a 100 mW XploRA PLUS confocal Raman microscope. The field-emission scanning electron microscopy was utilized to analyze the surface morphology of the samples (FESEM, Mira 3-XMU). The Jasco V-750 UV-Visible spectrophotometer was used to gather absorption spectra in the UV-visible region, extending from 190 to 900 nanometers.

## Results and Discussion

The microstructure of PEDOT: PSS may be inferred and described with X-ray diffraction (XRD) assistance. This method is also capable of determining the crystallinity level of the substance. Figure 1 displays the XRD patterns acquired from the PEDOT: PSS film that was the subject of this study. Within the PEDOT: PSS matrix, inter-chain ring stacking caused diffraction at about 2 theta= 16.90 degrees. The distances between the stacking [010] of the PEDOT: PSS chains are the cause of the high diffraction peaks at 2theta=28.45° and 42.25°. An X-ray diffraction examination was carried out, and the findings were comparable to those obtained for PEDOT: PSS, which was completely pure <sup>[19]</sup>.

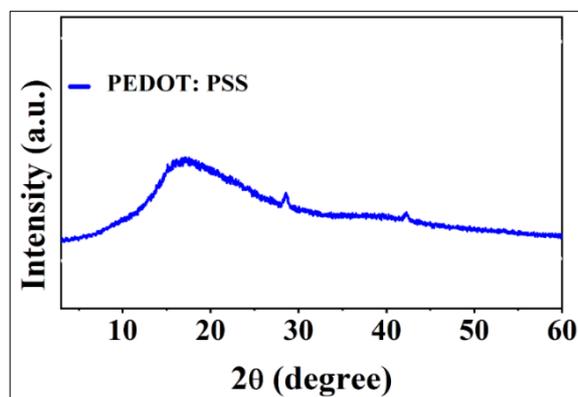


Fig 1: XRD pattern of PEDOT: PSS

Analyzing the vibration patterns of PEDOT: PSS matrices may be done with the use of FTIR measurements, which can then be used to determine the composition of the matrix. Figure 2 displays the FTIR spectra of PEDOT-PSS in its various forms. According to the results of the research conducted on the previously published material. The transmittance bands are seen in the FTIR spectra of PEDOT: PSS is located at  $2919\text{ cm}^{-1}$  and  $1498\text{ cm}^{-1}$ . These bands can

be ascribed to C-H stretching and C-O-H bending, respectively. A band at  $1239\text{ cm}^{-1}$ , which is the consequence of asymmetric BO stretching, can also be seen in the FTIR spectra of PEDOT: PSS film. The C-O stretching vibration is responsible for the transmission bands that may be found at  $1068\text{ cm}^{-1}$  and  $1020\text{ cm}^{-1}$ . It was determined that C-H shaking was the cause of the  $840\text{ cm}^{-1}$  transmittance bands that were seen <sup>[20]</sup>.

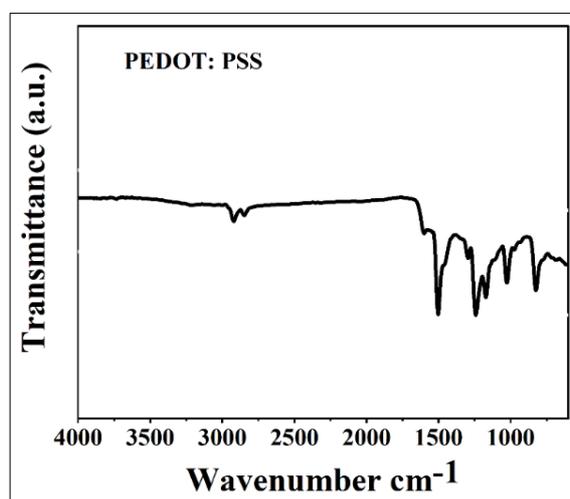


Fig 2: FTIR spectra of PEDOT: PSS

Figure 3 shows the UV-vis spectra of PEDOT's PSS, which has an absorption range of 190 to 900 nm. The UV absorbance at 261 nm in the absorption spectra of the PEDOT: PSS conducting polymer may be traced back to the

phenyl groups that PSS replaced. The wide bands between 500 and 700 nm might be created by  $\pi^*$  transitions in the thiophene ring. A free tail extending into the near-infrared region indicates that the PEDOT: PSS chains are doped <sup>[21]</sup>.

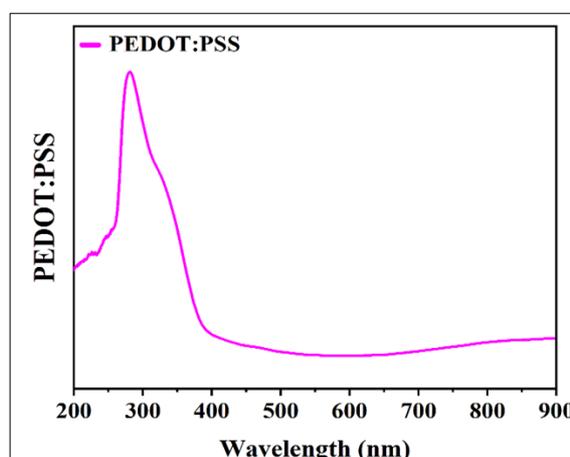


Fig 3: UV-Vis spectra of PEDOT: PSS

It is common practice to assess carbon compounds and conduct polymers using Raman spectroscopy, a potent instrument for analyzing the symmetric bond [22]. Figure 4 depicts the Raman spectra of PEDOT: PSS. PEDOT is to blame for the occurrence of a high-intensity band at 1430  $\text{cm}^{-1}$ . This band corresponds to the C = C symmetric

stretching vibration. The shoulder bands between 1400 and 1500  $\text{cm}^{-1}$  became much weaker when compared to PEDOT: PSS in its purest form. The bands in the PEDOT: PSS spectra situated at 714, 982, and 1,256  $\text{cm}^{-1}$  have been caused by symmetric C-S-C deformation, oxyethylene ring deformation, and C-C inter-ring stretching, respectively [23].

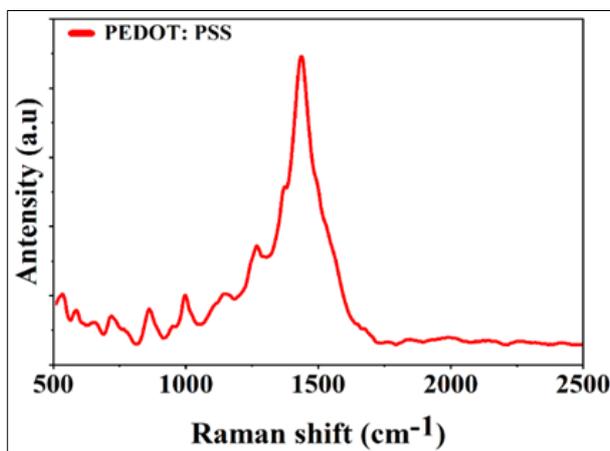


Fig 4: Raman spectra of PEDOT: PSS

Figure 5 depicts the conclusions that were gleaned from an AFM investigation into the part that the PSS matrix plays in deciding how the PEDOT latex would ultimately materialize. These photographs offer a topographical portrayal of an area of drop-cast PEDOT: PSS thin films that is three meters by three meters in size. Pure PEDOT: PSS has a surface that is, to a significant degree, free of

flaws, as can be seen in Figure 3a. This is the case because the surface is pure. Histograms showing the distribution of the particle heights of PEDOT: PSS demonstrate (Figure 3b) that the material almost fully meets the Gaussian distribution for particle height. This can be seen by looking at the distribution of the particle heights [24].

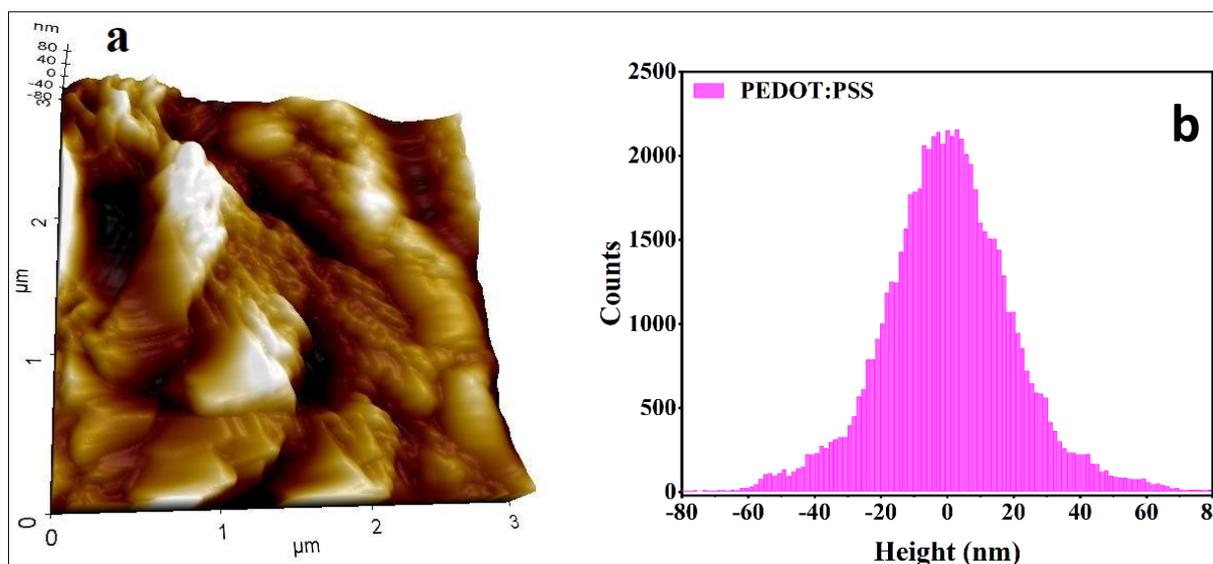
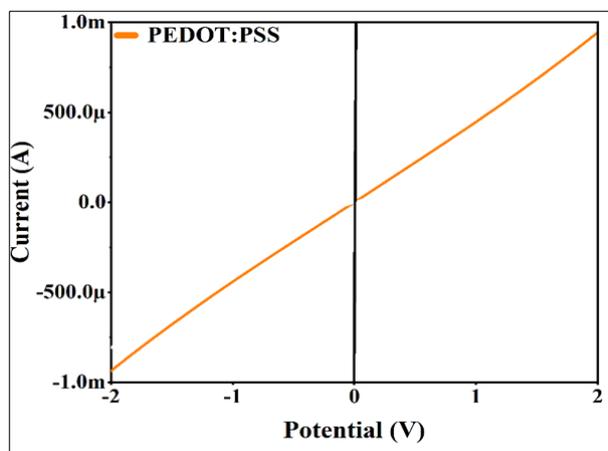


Fig 5: 3D AFM image and histogram of PEDOT: PSS

### Electrical properties measurements

A representation of the I-V characteristic of PEDOT: PSS is shown in figure 6: PSS. The I-V properties of the PEDOT: PSS material showed that it had a high conductivity as well as a linear current profile, with a maximum current of 0.9 mA when applied at a voltage of 2 V. The low work function of PEDOT: PSS, which shows a low barrier height

in the contact between the electrode surface and PEDOT: PSS, may be responsible for the high conductivity of the PEDOT: PSS. The inverse slope of the I-V curves served as the beginning point for the calculation that was done in order to calculate the resistances of the materials after they had been produced. It was discovered that the resistivity of PEDOT: PSS was 2.13 kΩ.



**Fig 6:** I-V characteristic of PEDOT: PSS

## Conclusion

In conclusion, the quality of this pure PEDOT-PSS system that was formed by just adjusting the experimental parameters gives a glimpse into the skills of an improviser and their potential to coax such a considerable change in characteristics out of that system. For the preparation of PEDOT: PSS, the in situ oxidative polymerization method was applied. In order to analyze the chemical structure and optical characteristics of the newly synthesized materials, several spectroscopic techniques such as X-ray diffractometry, UV-vis spectrophotometer, Fourier transform infrared spectroscopy, and Raman spectroscopy was utilized. In addition, an atomic force microscope was utilized to validate the morphological characteristics of the created materials. Finally, we found that the electrical charge carrier transport in PEDOT: PSS can be described by precipitation in a two-phase setup consisting of an Adsorbent PEDOT: PSS complex that is dissolved by the electrolyte PSS. This conclusion was reached as a result of our findings that the electric charge carrier transport in PEDOT: PSS can be described in this manner.

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