International Journal of Scientific Advances
ISSN: 2708-7972
Volume: 6 | Issue: 3 | May – Jun 2025 Available Online: www.ijscia.com
DOI: 10.51542/ijscia.v6i3.23

Evaluation of the Addition of O-Toluidine and Nano-Ag on The Optical and Electrical Properties of PEDOT-PSS Polymer

Nadhim A. Abdullah, Abdullah A. Hussein*, Ghufran M. Shabeeb, and Haider Abdulelah

Department of Materials Science, Polymer Research Centre, University of Basrah, Iraq

*Corresponding author details: Abdullah A. Hussein; Abdullah.hussein@uobasrah.edu.iq

ABSTRACT

In this work, we investigate the optical and electrical properties of PEDOT-PSS:PVA:POT and PEDOT-PSS:PVA:POT:AgNPs thin films, by adding different concentrations of POT (1, 5, and 9 v%). The thin films were deposited using the spin coating method. UV-Vis spectroscopy was used to inspect the structure of the created tests. Transmittance estimations were conducted within the wavelength range of 200-900 nm to calculate the optical energy gap. The results showed that the absorption and energy bandgap decreased with the addition of Ag and different ratios of POT, while the electrical conductivity decreased in the presence of Ag. The electrical conductivity values were (2.28×10-9, 2.57×10-9, and 2.99×10-8) S.cm-1 for PEDOT-PSS:PVA:POT and (2.9×10-7, 1.04×10-6, and 4×10-7) S.cm-1 for PEDOT-PSS:PVA:POT:AgNPs.

Keywords: O-toluidine; PEDOT-PSS; PVA; POT; Silver Nanoparticle.

INTRODUCTION

PEDOT:PSS encompasses a complex structure due to the combination of two polyelectrolytes. The chemical structures of PEDOT:PSS and to balance the charge of the carriers in conjugation with the conjugated poly(3,4-ethylene dioxythiophene) (PEDOT) and the poly(styrene sulfonate) (PSS) have appeared in Figure 1.[1] Based on the picture, we can say that. 1b, the -OH groups in the PSS structure separated to release H+ in water, and then the H+ specifically reacted with the double bond in the PEDOT's thiophene, resulting in the creation of hydrogen bonding. At the same time, the electrons in the C-O electron pairs were pulled towards O because O has a stronger pull on these electrons.

In simpler terms, according to the information shown in the diagram. In simple words; The -OH groups in the PSS structure separated and released H+ in water. Then, the H+ specifically attacked the double bond in the PEDOT's thiophene, resulting in the creation of hydrogen bonding. At the same time, the electrons of the C-O shared pairs were pulled towards O because it is more electronegative. This situation happened because the C in the C-O bond had turned into a positive charge. An ionic bond formed when the positively charged C+ and negatively charged O- of the PSS structures came together.[2] Also, the arrangement of atoms in PEDOT:PSS can be seen in the picture shown in figure The substance 1c, when mixed with water, forms small gel particles. These particles create films with different sections: some are blue and rich in PEDOT: PSS, while others are grey and rich in PSS. Tiny parts of PEDOT are touching the PSS bundles when they are mixed together in a liquid form.

Furthermore, we can analyze the chemical structure of PEDOT:PSS by comparing it with the morphological model shown in Figure 1c. This text basically says that when 1c is mixed with water, it forms tiny gel particles. These particles create films that have two types of structures: blue areas with a lot of PEDOT: PSS and grey areas with a lot of PSS. Tiny pieces of PEDOT come into contact with the PSS bundles when they are mixed together in a liquid. This observation causes the creation of a mixture of gel particles in water. This happens because the two components have different weights and this makes one of them have a larger density. The typical weight of one molecule of PEDOT is around 1000 grams per mole, while the weight of one molecule of PSS is around 400,000 grams per mole [3].

This observation causes gel particles to form a colloid in water. This happens because the two parts have different weights and this causes them to have different densities. The average weight of PEDOT is about 1000 grams per mole, and the weight of PSS is about 400,000 grams per mole. In this situation, the Ag NPs helped to cover the conducting polymer. This improved the electrical performance by combining the metal core with the conductor polymer shell. The way electricity passes through something showed that bigger particles made it easier for electricity to flow. Two ideas can possibly explain the outcome. First, when silver particles were formed, they prevented PEDOT from combining with PSS, causing

the PEDOT chains take on a different shape that is more capable of conducting electricity, similar to a quinoid form. Second, PSS is a material that stops the movement of charged particles through the conductive PEDOT chains. The problem can be solved by using a combination of PSS and Ag+.

The silver nanoparticles act as connections between the isolated PSS chains and the conductive PEDOT chains. Also, it has been said that having Ag NPs on the PEDOT:PSS provides the least amount of resistance. This means that the electrons can move quickly through the PEDOT:PSS/Ag film, which is good for making supercapacitors [4]. The silver nanoparticles mixed with PEDOT:PSS became more conductive. This makes them very useful as a layer in solar cells. This information is based on a study cited as [5].

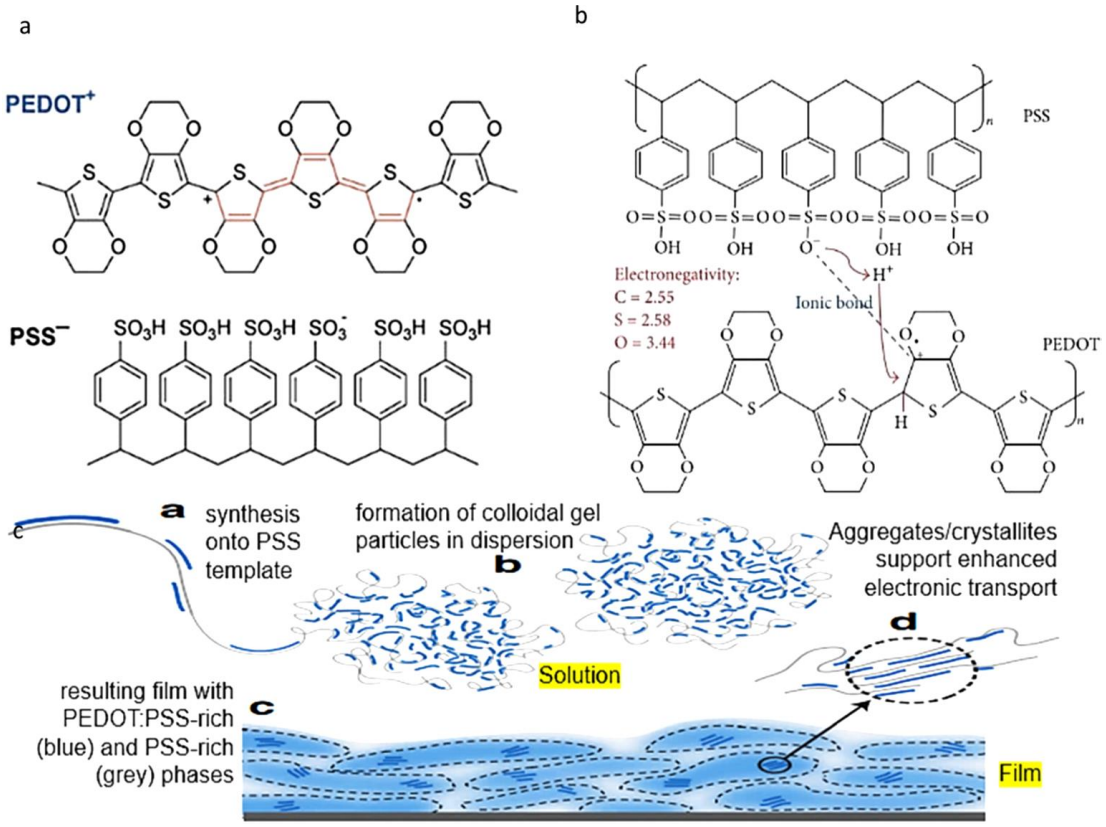


FIGURE 1: The (a) chemical structure, (b) response, and (c) morphological plot of PEDOT and PSS.[6-7]

Poly (3,4-ethylenedioxythiophene): Poly (styrene sulfonate) (PEDOTPSS) has been demonstrated to be a surprising conducting polymer due to its tremendous application and purposes in various gadgets. PEDOT: PSS is broadly utilized in, but not restricted to, sun-based cells, thermoelectric gadgets, sensors, fuel cells, carbon-capturing layers, and supercapacitors .[8-15] Its far-reaching commonsense applications are ascribed to its one-of-some-kind properties. PEDOT:PSS being a water solvent is commercially accessible as a fluid scattering with distinctive conductivity grades, and thus can effortlessly frame great uniform lean films by utilizing diverse planning strategies .[16-20]

PEDOT:PSS is a material that conducts electricity well and also has a high work function. It is transparent to light in the visible range, meaning you can see through it. This makes it a good option for use as a middle layer or in electrodes in devices that use both electricity and light. Additionally, the electrical and optical properties of this material can be easily adjusted using simple chemical processes or by adding substances to it. Various additional treatments can also be done to modify these properties.[21]

PEDOT: PSS is a material that conducts electricity well and is also transparent, allowing light to pass through. Because of these properties, it can be used as a layer or electrode in devices that use both electricity and light. Additionally, this material's electrical and optical properties can be easily adjusted by using basic chemical or additive techniques and different post-treatments [19, 22-23].

MATERIALS AND METHODS

Materials

PEDOT:PSS water dispersion is a conducting conjugated polymer purchased from Sigma-Aldrich. It sounds like the material you are referring to is a highly conductive conjugate polymer mixture dispersion that can result in polymeric films with significant electrical conductivity when specific additives like dimethyl sulfoxide (DMSO) or ethylene glycol are included in the solution. The post-baking process at 125°C for 20 minutes seems to be crucial for achieving the desired conductivity levels. Polyvinyl alcohol (PVA)), which is a low-cost polymer, highly transparent, and water-soluble was obtained from HiMedia Laboratories Pvt. Ltd (Mw14000 g/mol, 99% hydrolyzed). The used poly

O-Toluidine from Thomas Baker chemicals (Mw 212.3 g/mol) PVT in India as reserved.

The silver nano-particles (AgNPs) were prepared through electrochemical method in this study by using Ag rods with 99.99% purity as electrodes in this process.

Silver nanoparticles Preparation

To prepare AgNPs by the electrochemical method, two Ag rods were placed in 120 ml of distilled water. Both Ag rods were supplied with 18 V by a DC voltage source. The total preparation time was 3 h at room temperature. After completing the preparation process, a salivary color solution was obtained, which was kept at a dark place for future use. A colorless solution with black deposits appeared as in Figure (1). The silver concentration (part per million (ppm)) of the prepared solution was estimated by the total-dissolved solid gauge.

The morphology and shape of the prepared AgNPs were studied using a NovaSEM 450 scanning electron microscope (SEM; FEI Co.).

Field Emission Scanning Electron Microscope (FE-SEM-Model: INSPECT F50, FEI company, USA) was used to specifying the grain size of AgNPs.[24]

Sample preparation

PVA solutions were prepared by dissolving in purified water at a concentration of 30 mg ml−1, similar to the concentration of the PEDOT: PSS solution. The PVA was dissolved by stirring for 4 hours at 95°C. Once the PVA was completely dissolved, the PEDOT: PSS dispersion, with 5% POT: AgNPS as an additive, was added to the desired weight ratio, and the solution was stirred for an additional 24 hours at room temperature. Various blend solutions were created, with the PEDOT: PSS content ranging from 1, 5, and 9 v%.

The Aluminum electrodes were deposited using a mechanical shadow mask,(2 × 2 cm2) electrodes organized perpendicularly to the spray-deposited PEDOT:PSS:PVA: AgNPS blend film, with a separation of 1cm between adjacent electrodes.

Measurements

The field emission scanning electron microscope (FE-SEM, FEI company, USA, Model: INSPECT F50) was utilized to analyze the forms and arrangements of AgNPs.

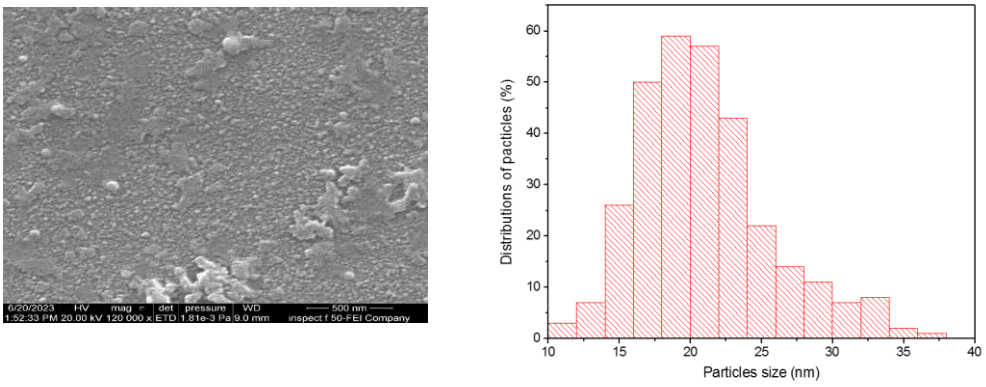
The samples (10mg) were sealed in aluminum pans under a nitrogen atmosphere by keeping the flow rate of 30 ml/min, in a temperature range between 0 up to 300°C and a heating rate of 20°C/min. The melting and degradation temperatures of the samples were determined.

RESULT AND DISCUSSION

Optical properties

The depiction in Figure 2(a) it is clear that AgNPs particles were dispersed and grown within deionized water. Figure 2(b) indicates that around 60% of the produced particles have an average diameter ranging between 15 - 25 nm, which represents the most common size range of AgNPs in this particular sample.

The optical properties of the thin films of the pristine PEDOT:PSS:PVA: POT (1,5,9 v%) and PEDOT:PSS:PVA:POT: AgNPs (1%,5%,9%) were investigated using the UV-visible spectroscopy. The absorption spectra of the films are shown in Figures 3 and 4 respectively.



(a) **(b)**

FIGURE 2: FE-SEM of AgNPs and distribution particles.

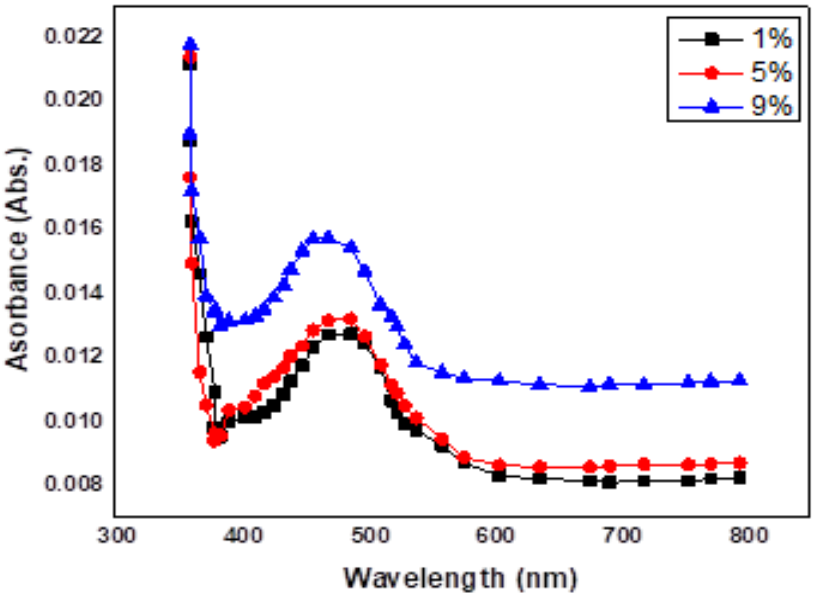


FIGURE 3: UV-VIS spectrum of PEDOT:PSS:PVA: POT.(1%,5%,9%).

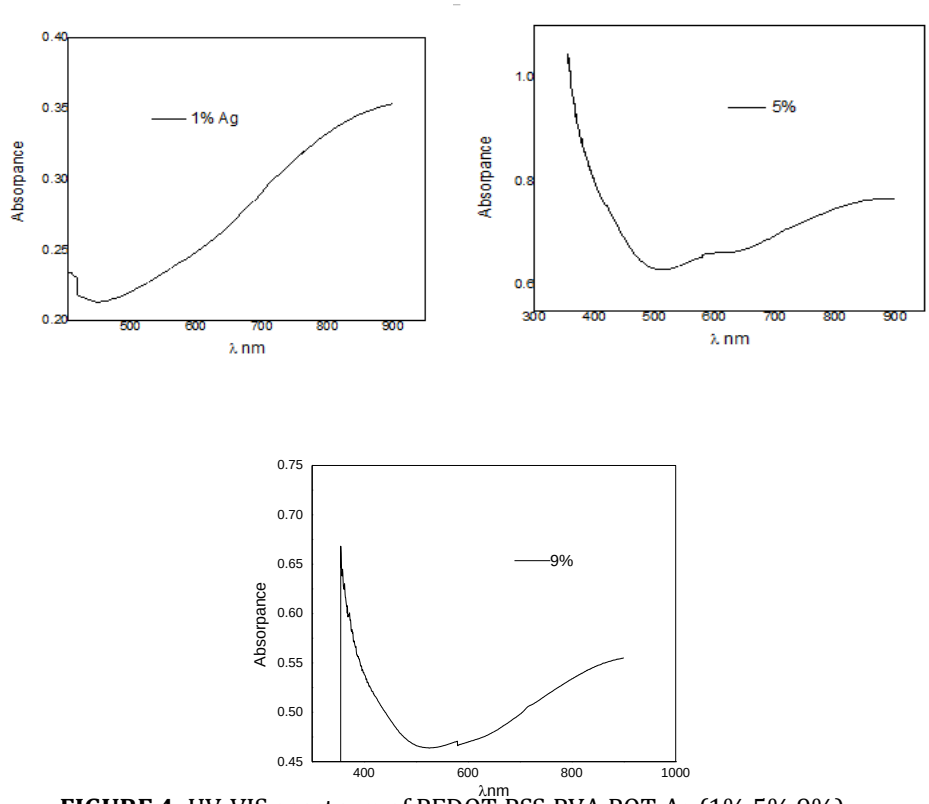


FIGURE 4: UV-VIS spectrum of PEDOT:PSS:PVA:POT:Ag (1%,5%,9%).

The optical properties of PEDOT:PSS:PVA:POT and PEDOT:PSS:PVA:POT:Ag thin films were examined utilizing UV-visible spectroscopy. The assimilation spectra of the films have appeared in Figure 3 (abc), which appears three major assimilation crests at (396, 420, 713) nm at the proportion POT(1%), (443, 579, 606) nm at the proportion POT(5%) and (422, 446, 585) nm at the ratio POT(9%).

The peak at 396 nm happens because of a change in the PEDOT structure, and the peak at 446 nm is related to a different type of change in structure. Also, the absorption spectrum at 579 nm matches the wavelength where the majority of the polymers absorb the most. The optical band gap, absorption coefficient, and energy of the incident photon are related to each other. The peak at 396 nm is caused by a change in the structure of the PEDOT backbone, while the peak at 446 nm is due to another type of transition called polaron-π* transition. Additionally, the absorption patterns at 579 nm align with the wavelength at which polymers absorb the most. The relationship between the optical band gap, absorption ability, and energy of the incoming photon is explained in [25-26].

Additionally, the absorption spectra at 579 nm match the wavelength at which the majority of the polymers absorb the most. We can understand the connection between the optical band gap, absorption coefficient, and energy of the photon [26, 27].

The connection between the optical band gap, absorption coefficient, and energy of the incoming photon is explained in [27-28].

$$\alpha h\nu = B(h\nu - Eg)r \quad \text{---------- (4)}$$

In simpler words, this text is talking about a formula. It mentions different values variable called (r) based on the type of electric transitions that cause light to be absorbed. The formula also includes an optical energy gap (Eg), a constant (B), and the value of (r) being 1/2, 3/2, 2, or 3. Specifically, it says that when (r) is 3/2, it refers to forbidden direct transitions, and when (r-2), it refers to indirectly allowed transitions.

The energy difference in the bands of the materials PEDOT:PSS:PVA:POT and PEDOT:PSS:PVA:POT:Ag changes depending on the thickness of the films. For PEDOT:PSS:PVA:POT, the band gap energies are 3.15 eV, 2.92 eV, and 1.41 eV for different film thicknesses.

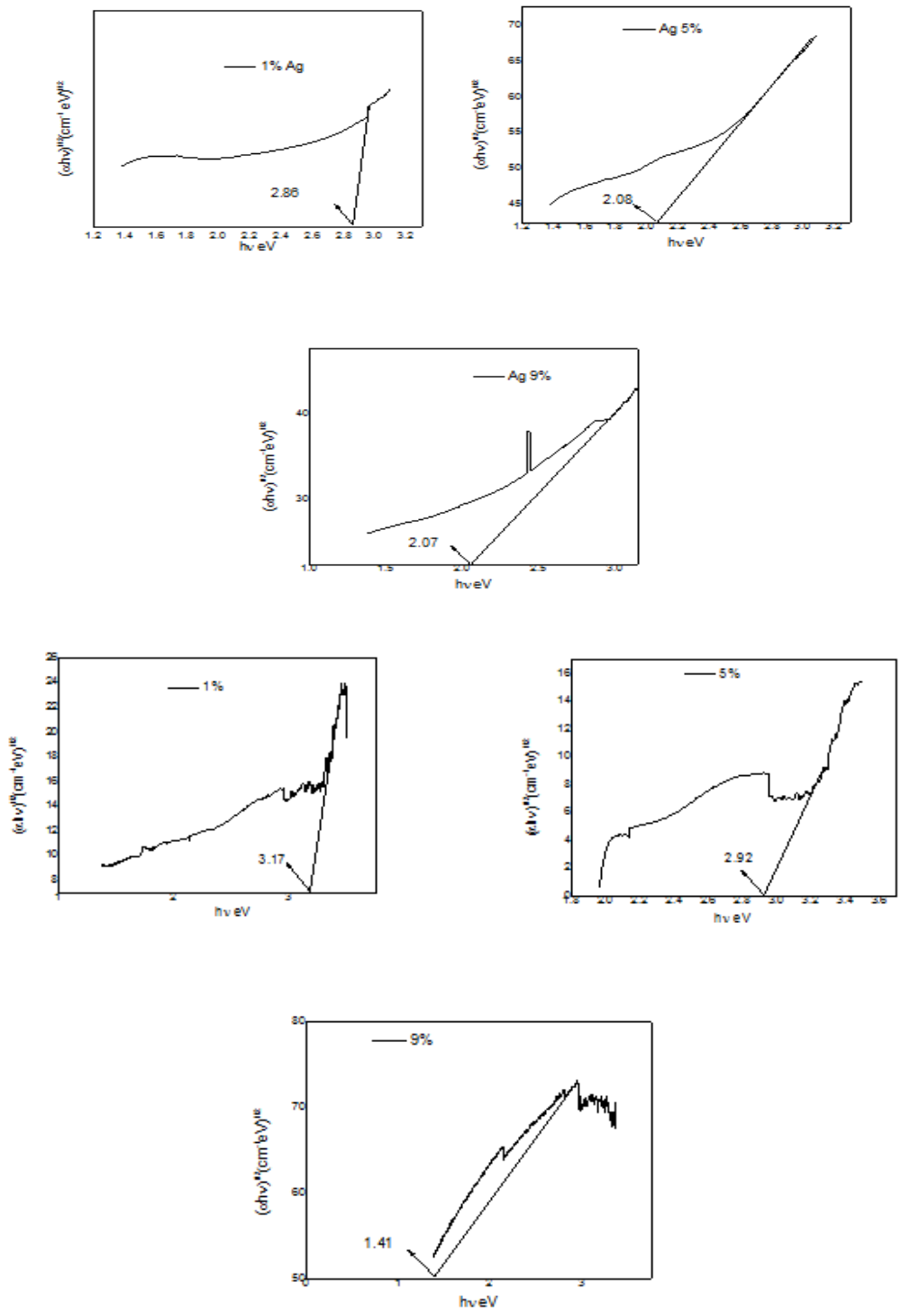


FIGURE 5: Shows the relation between (αhν)1/2 and hν for PEDOT:PSS:PVA:POT:Ag.

On the other hand, for PEDOT:PSS:PVA:POT:Ag, the band gap energies are 2.86 eV, 2.08 eV, and 2.07 eV for different film thicknesses.

We can figure out the energy gap (Eg) of a semiconductor by using the classical formula for optical absorption near the edge. This formula shows the relationship between the square root of the absorption coefficient times the energy of a photon, and the energy of the photon itself. The results are shown in Figure 5 for all types of films. The determined band gap values are obtained by extending the linear part of the graph where the square root of (αhν) is equal to 0. The range of the allowed indirect transition optical gap is between 1.41 eV and 3.17 eV for PEDOT:PSS:PVA:POT, and between 2.86 eV and 2.07 eV for PEDOT:PSS:PVA:POT:Ag.

Electrical conductivity

Electrical conductivity was measured for PEDOT:PSS:PVA:POT and PEDOT:PSS:PVA: POT:Ag, the results showed that PEDOT:PSS:PVA:POT has a conductivity value of $2.28x10^{-9}$, $2.57\ x10^{-9}$ $299\ x10^{-9}$ ($S.cm^{-1}$) at room temperature, while PEDOT: shown in the figure 6 for all ratios. The current-voltage curves for PEDOT: PSS:PVA:POT:Ag are shown in Figure 7.[30] PSS:PVA:POT:Ag is estimated to be $2.9\ x10^{-7}$ $10\ x10^{-6}$ $4x10^{-7}$($S.cm^{-1}$) at room temperature as shown in Figure 7.

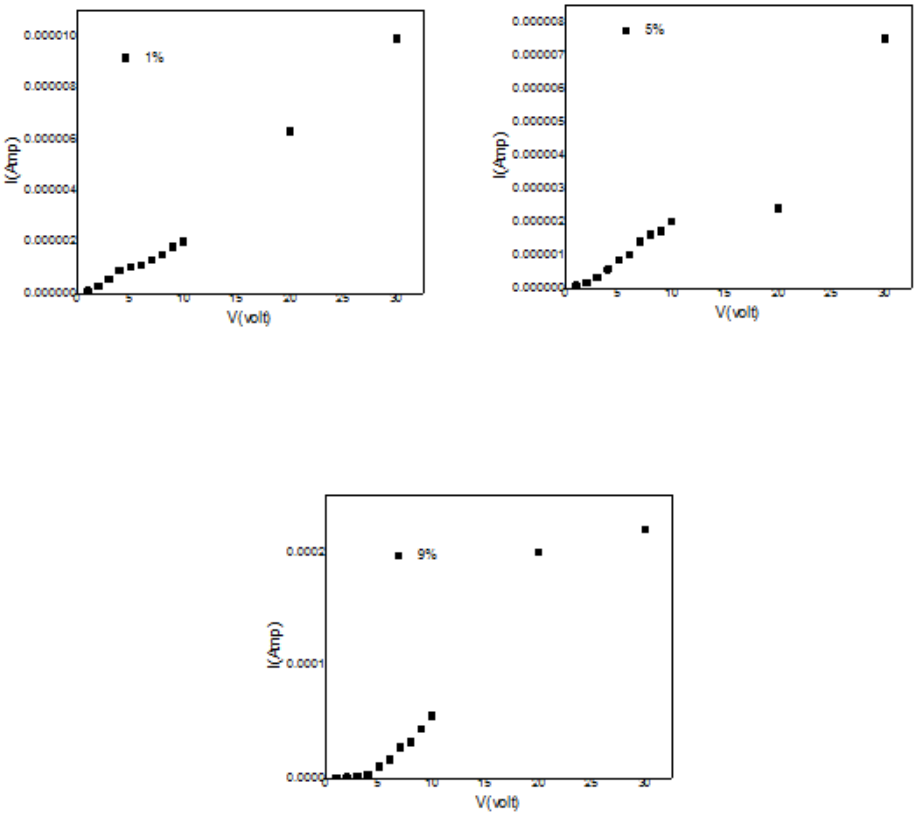


FIGURE 6: shows Current-voltage curve for PEDOT:PSS:PVA:POT.

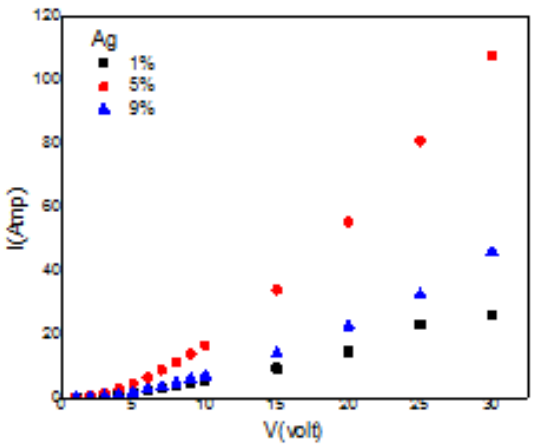


FIGURE 7: The current-voltage curve for PEDOT:PSS:PVA:POT:Ag.

CONCLUSION

This work centers on considering a shifting of the optical and electrical properties of PEDOT-PSS:PVA:POT and PEDOT-PSS:PVA:POT:Ag blend by means of an including of a diverse proportion of POT (1%, 5%, and 9%) v/v, lean films were kept utilizing cast strategy. The structure of the manufactured tests was inspected with UV-Vis spectroscopy.

The optical properties of the flawless PEDOT:PSS:PVA:POT and PEDOT:PSS:PVA:POT:Ag were explored. These things have uncovered that the vitality bandgap was found diminishing with the expansion of Ag and a distinctive proportion of POT, moreover, the electrical conductivity diminished in a display of Ag. It was (2.28×10^{-9}, 2.57×10^{-9}, and 2.99×10^{-8}) $S.cm^{-1}$ for PEDOT-PSS:PVA:POT and (2.9×10^{-7}, 1.04×10^{-6}, and 4×10^{-7}) $S.cm^{-1}$ for PEDOT-PSS:PVA:POT:Ag.

REFERENCES

[1] N. A. Shahrim, Z. Ahmad, A. W. Azman, Y. F. Buys, and N. Sarifuddin, Mechanisms for doped PEDOT:PSS electrical conductivity improvement, Mater. Adv., 2, 7118-7138, (2021).

[2] O. P. Dimitriev, D. A. Grinko, Y. V. Noskov, N. A. Ogurtsov, and A. A. Pud, PEDOT:PSS films-Effect of organic solvent additives and annealing on the film conductivity, Rev. Mat. Adv. 7136., Synth. Met., 159, 2237-2239, (2009).

[3] S. Khasim, A. Pasha, A. S. Roy, A. Parveen, and N. Badi, Effect of Secondary Doping Using Sorbitol on Structure and Transport Properties of PEDOT–PSS Thin Films, J. Electron. Mater, 46, 4439-4447, (2017).

[4] D. S. Patil, S. A. Pawar, J. Hwang, J. H. Kim, P. S. Patil, and J. C. Shin, Silver incorporated PEDOT: PSS for enhanced electrochemical performance, J. Ind. Eng. Chem., 42, 113-120, (2016).

[5] A. Iwan, B. Boharewicz, I. Tazbir, A. Sikora, and B. Zboromirska-Wnukiewicz, Silver Nanoparticles in PEDOT: PSS Layer for Polymer Solar Cell Application, Int. J. Photoenergy, 1-9, 2015.

[6] S. Arora, V. Singh, M. Arora, and R. Pal Tandon, Evaluating effect of surface state density at the interfaces in degraded bulk heterojunction organic solar cell, Phys. B Condens. Matter., 407, 3044-3046, (2012), https://doi.org/10.1016/ j.physb.2011.08.086.

[7] V. Singh, S. Arora, M. Arora, V. Sharma, and R.P. Tandon, Characterization of doped PEDOT:PSS and its influence on the performance and degradation of organic solar cells, Semicond. Sci. Technol.,29,(2014), https://doi.org/10.1088 /02681242/29/4/045020.

[8] K. Sun, S. Zhang, P. Li, Y. Xia, X. Zhang, D. Du, F.H. Isikgor, and J. Ouyang, Review on application of PEDOTs and PEDOT:PSS in energy conversion and storage devices, J. Mat. Sci. Mat. Electron., 26, 4438-4462, (2015), https://doi.org/ 10.1007/s10854-015-2895-5.

[9] J.H. Lee, J.P. Jung, E. Jang, K.B. Lee, Y.J. Hwang, B.K. Min, and J.H. Kim, PEDOT-PSS embedded comb copolymer membranes with improved CO2 capture, J. Memb. Sci., 518, 21-30, (2016), https://doi.org/10.1016/j.memsci.2016.06.025.

[10] Y. Meng, M. Ahmadi, X. Wu, T. Xu, L. Xu, Z. Xiong, and P. Chen, High performance and stable all-inorganic perovskite light emitting diodes by reducing luminescence quenching at PEDOT:PSS/Perovskites interface, Org. Electron., 64, (2019), https://doi.org/10.1016/j.orgel. 2018.10.014.

[11] Q. Meng, Q. Jiang, K. Cai, and L. Chen, Preparation and thermoelectric properties of PEDOT:PSS coated Te nanorod/PEDOT:PSS composite films, Org. Electron., 64, (2019), https://doi.org/10.1016/j.orgel.2018.10.010.

[12] B. Baruah, and A. Kumar, PEDOT:PSS/MnO2/rGO of organic solvent additives and annealing on the film conductivity, Rev. Mat. Adv. 7136., Synth. Met., 159, 2237-2239, (2009).

[13] S. Khasim, A. Pasha, A. S. Roy, A. Parveen, and N. Badi, Effect of Secondary Doping Using Sorbitol on Structure and Transport Properties of PEDOT–PSS Thin Films, J. Electron. Mater, 46, 4439-4447, (2017).

[14] D. S. Patil, S. A. Pawar, J. Hwang, J. H. Kim, P. S. Patil, and J. C. Shin, Silver incorporated PEDOT: PSS for enhanced electrochemical performance, J. Ind. Eng. Chem., 42, 113-120, (2016).

[15] A. Iwan, B. Boharewicz, I. Tazbir, A. Sikora, and B. Zboromirska-Wnukiewicz, Silver Nanoparticles in PEDOT: PSS Layer for Polymer Solar Cell Application, Int. J. Photoenergy, 1-9, 2015.

[16] S. Arora, V. Singh, M. Arora, and R. Pal Tandon, Evaluating effect of surface state density at the interfaces in degraded bulk heterojunction organic solar cell, Phys. B Condens. Matter., 407, 3044-3046, (2012), https://doi.org/10.1016/ j.physb.2011.08.086.

[17] V. Singh, S. Arora, M. Arora, V. Sharma, and R.P. Tandon, Characterization of doped PEDOT:PSS and its influence on the performance and degradation of organic solar cells, Semicond. Sci. Technol.,29,(2014), https://doi.org/10.1088 /0268- 1242/29/4/045020.

[18] K. Sun, S. Zhang, P. Li, Y. Xia, X. Zhang, D. Du, F.H. Isikgor, and J. Ouyang, Review on application of PEDOTs and PEDOT:PSS in energy conversion and storage devices, J. Mat. Sci. Mat. Electron., 26, 4438-4462, (2015), https://doi.org/ 10.1007/s10854-015-2895-5.

[19] J.H. Lee, J.P. Jung, E. Jang, K.B. Lee, Y.J. Hwang, B.K. Min, and J.H. Kim, PEDOT-PSS embedded comb copolymer membranes with improved CO2 capture, J. Memb. Sci., 518, 21-30, (2016), https://doi.org/10.1016/j.memsci.2016.06.025.

[20] Y. Meng, M. Ahmadi, X. Wu, T. Xu, L. Xu, Z. Xiong, and P. Chen, High performance and stable all-inorganic perovskite light emitting diodes by reducing luminescence quenching at PEDOT:PSS/Perovskites interface, Org. Electron., 64, (2019), https://doi.org/10.1016/j.orgel. 2018.10.014.

[21] Q. Meng, Q. Jiang, K. Cai, and L. Chen, Preparation and thermoelectric properties of PEDOT:PSS coated Te nanorod/PEDOT:PSS composite films, Org. Electron., 64, (2019), https://doi.org/10.1016/j.orgel.2018.10.010.

[22] B. Baruah, and A. Kumar, PEDOT:PSS/MnO2/rGO ternary nanocomposite-based anode catalyst for enhanced electro-catalytic activity of methanol oxidation for direct methanol fuel cell, Synth. Met., 245, 74-86, (2018), https://doi.org/ 10.1016/j.synthmet.2018.08.009.

[23] S.B. Singh, T. Kshetri, T.I. Singh, N.H. Kim, and J.H. Lee,EmbeddedPEDOT:PSS/AgNFs network flexible transparent electrode for solid-state super-capacitor, Chem. Eng. J., 359, 197-207, (2019),https://doi.org/10.1016/j.cej.2018.11.160.

[24] G.-E. Kim, D.-K. Shin, J.-Y. Lee, and J. Park, Effect of surface morphology of slot-die heads on roll-to-roll coatings of fine PEDOT:PSS stripes, Org. Electron., 66, 116-125, (2019), https://doi.org/ 10.1016/ j.orgel.2018.12.033.

[25] C. Koidis, S. Logothetidis, C. Kapnopoulos, P.G. Karagiannidis, A. Laskarakis, and N.A. Hastas, Substrate treatment and drying conditions effect on the properties of roll-to-roll gravure printed PEDOT:PSS thin films, Mater. Sci. Eng., B. 176, 1556-1561,(2011),https://doi.org/10.1016/j. mseb.2011.03.007.

[26] J. Griffin, A.J. Ryan, and D.G. Lidzey, Solution modification of PEDOT:PSS inks for ultrasonic spray coating, Org. Electron., 41, 245-250, (2017), https://doi.org/10.1016/j.orgel.2016.11.011.

[27] B.-J. Kim, S.-H. Han, and J. S. Park, Properties of CNTs coated by PEDOT:PSS films via spin-coating and electrophoretic deposition methods for flexible transparent electrodes, Surf. Coatings Technol., 271, 22-26, (2015), https://doi.org/ 10.1016/j.surfcoat.2015.01.045.

[28] F. Zabihi, Y. Xie, S. Gao, and M. Eslamian, Morphology, conductivity, and wetting characteristics of PEDOT:PSS thin films deposited by spin and spray coating, Appl. Surf. Sci., 338, 163-177,(2015), https://doi.org/10.1016/ j.apsusc. 2015.02.128.

[29] A.K. Sarker, J. Kim, B.-H. Wee, H.-J. Song, Y. Lee, J.-D. Hong, and C. Lee, Hydroiodic acid treated PEDOT:PSS thin film as transparent electrode: an approach towards ITO free organic photovoltaics, RSC Adv., 5, 52019-52025, (2015), https://doi.org/10.1039/C5RA07136D.

[30] Y.H. Kim, C. Sachse, M.L. Machala, C. May, L. Muller-Meskamp, and K. Leo, Highly conductive PEDOT:PSS electrode with optimized solvent and thermal post treatment for ITO-free organic solar cells, Adv. Funct. Mater., 21, 1076-1081, (2011),https://doi.org/10.1002/adfm.201002290.

[31] Y. Xia, and J. Ouyang, PEDOT:PSS films with significantly enhanced conductivities induced by preferential solvation with co-solvents and their application in polymer photovoltaic cells, J. Mater. Chem., 21, 4927, (2011) https://doi.org/ 10.1039/c0jm04177g.