

Structure and Electrical Properties of ZnO Nanoparticles Blend with POT-DBSA

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Abstract. In this study, we report on a successful preparation nanocomposites poly(o-toluidine) (POT) doping with dodecylbenzene sulfonate acid (DBSA)/ ZnO by in-situ polymerization of (o-toluidine) monomer using ZnO nanoparticles with the weight ratios OT/ZnO: 1/5%, 1/10%, 1/15%. The composite films have been prepared by using the casting method on the different substrates depending on the type of measurement. The surface morphology of the prepared samples was studied by the field emission scanning electron microscopy (FESEM). The results of FESEM indicate that ZnO nanoparticles were successfully embedded in the POT via chemical interactions between ZnO and (O-toluidine) monomer and the EDX spectrum showed the presence of element Zn in POT-DBSA/ZnO composites. The crystal structure was measured by x-ray directional and pattern revealed the presence of ZnO in dopant polymer, in the diffraction the patterns of POT-DBSA. The intensity of the peaks was increased as the amount of ZnO nanoparticles increased in POT-DBSA. The typical rectifying behavior indicated that the formation of a diode observes by the I–V characterization of POT-DBSA/ZnO composites at a thin film layer with top Al thin layer contact.

1. Introduction

Polymers are usually used as insulating and structural materials in packaging and electrical insulations. Combining the advantages of traditional polymers, such as ease of manufacture, lightweight, and low cost, with the characterization of semiconductors and metals, has been the focus of researchers in the industrial fields for the past few decades. In 1977, Heeger, et al[1] obtained on the high conductivity of polyacetylene by doping with I₂, Br₂. or AsF₅. After that, a variety of other conducting polymers and their derivatives have been discovered[2, 3]. Conjugation in polymers enables some of the π -electrons to be delocalized and shared throughout the polymer. The delocalized electrons may move around the entire system and become the charge carriers that make the polymer conductive. Conductivity in polymers can be divided into two types: i) composites conductivity, which is done by adding conducting particles (metallic) to an insulating polymer chain that can be achieved by synthetic method or blending method[4] and ii) conductivity by oxidation/reduction the process creates charge carriers in the form of polarons (radical ions), bipolarons (dications or dianions), or solitons in the polymer[5]. The conducting polymers can be prepared by electrochemical or chemical methods. Poly (o-toluidine) is one of the most promising substituted polyaniline (PANI)[6-8]. It is an electroconductive polymer, good chemical stability, easily polymerization that has several technological applications[9-11]. PANI has hampered its industrial applications due to it have not solubility, poor mechanical properties, and low processability. Therefore, to solve this problem of poor chemical and mechanical properties of polyaniline in many applications, a considerable amount of work has been done to prepare incorporation conducting polymer with other particles[12-17]. Also, the dopant POT with dodecylbenzene sulfonate (DBSA) could be soluble in many common solvents[18, 19]. DBSA has

several industrial applications such as an emulsifier for agricultural herbicides, in emulsion polymerization and as a coupling agent[20]. Composites or nanocomposites of the conducting polymer with other nanoparticles[12, 13, 21] used to solve the many problems in the conducting polymers. Nano ZnO an important semi conductive oxide structure material with a direct wide bandgap (3.37 eV)[22]. The major interaction of POT–DBSA/ ZnO nanocomposite an insulating and structural material on the surface area as the size of ZnO nanoparticles decreases, the surface to volume ratio and the specific area safely increase. The relatively high surface area is highly beneficial for the use of POT–DBSA/ ZnO nanocomposite.

In this work, we have synthesized poly (o-toluidine) doped with dodecylbenzene sulfonate (POT-DBSA) by in-situ chemical oxidative polymerization method. The monomer (OT-DBSA) was used in composites with different weight ratios of ZnO nanoparticles structural by the same method. The effect of different weight ratios of ZnO nanoparticles on the electrical and structural properties of the polymer has been studied. By using many analytical techniques.

2. Experimental

2.1. Synthesis of poly-o-toluidine- dodecyl benzene sulfonic acid (POT-DBSA)

The polymerization of o-toluidine monomer was carried out at 0–5 °C by the addition of 1.7 gm of o-toluidine(Fisher scientific company, USA)into 1M of HCl(Fluka company, USA) contain 5.8 gm of DBSA(Sigma Aldrich, USA) with continuous stirring for 30min. APS (5.2 gm)(NH₄)₂S₂O₈(Sigma Aldrich, USA), as an initiator dissolved in 1M of HCl was slowly poured into the polymerization bath through 30min and polymerization solution was left for 24 h with continuous stirring, a green colour edge was obtained[23-25]. The POT precipitated was filtrated and washed with excess amount of distilled water to remove excess of impurities. The powder of POT-DBSA was then dried at 70 °C for 6 h.

2.2. Preparation of POT-DBSA/ ZnO composites

Amount of o-toluidine were added to 10 mL was adjusted to about 1 mol/L by HCl. The solution was stirred for 10 min and then a (5,10, and 15 wt%) of ZnO (MK Nano Canada) was added to it, followed by the addition of DBSA (5.2) gm in 11 ml (1M HCl). The autoclave was sealed and kept at 140 °C for 4 h. The mixture was stirred for 30 min at room temperature. The addition of APS (5.2 gm) in (120 ml, 1M HCl) at a weight ratio ZnO to OT of (5%, 10, and 15%) at 0-5 °C. The mixture was kept at room temperature for 24 h under stirrer. The precipitates were washed by deionized water, for several times, and then dried at 60 °C in an oven.

2.3. Characterization and measurements techniques

The POT-DBSA and nanocomposites dissolved in chloroform (Sigma Aldrich, USA.) thin films were synthesized by the Following conditions (at 2000 rPs per min) on the interdigitated finger electrode using mothed of spin coating, (Backer lab equipment, VE135n Model). The FESEM and EDX measurements, POT samples were carried out using Leo-Supra 50vp (Carl Zeiss, Germany) equipped with an EDX system. X-ray diffraction (XRD) scans were carried out using the Schimadzu-7000 diffractometer at room temperature in the Bragg angle (2theta) (5–80°). The conductivity (σ) of these films was measured by a finger probe method and Al electrodes as shown in Fig 1, using Keithley Series 2400 Source Meter. The electrical conductivity (σ)was calculated from the following equation 1 [26]:

$$\sigma s = \left[\frac{I}{V} \right] \left[\frac{L}{Wt} \right] \quad (1)$$

Where t is the thickness of the thin film, W is the distant fingers (10mm), ℓ is the number of fingers is to be (10), and L is the space between electrodes (100 μ m).

The resistance of POT samples was obtained from the slope of current-voltage curves. Schottky diodes of films were fabricated by using Al electrodes and characterized by measuring I–V curves.

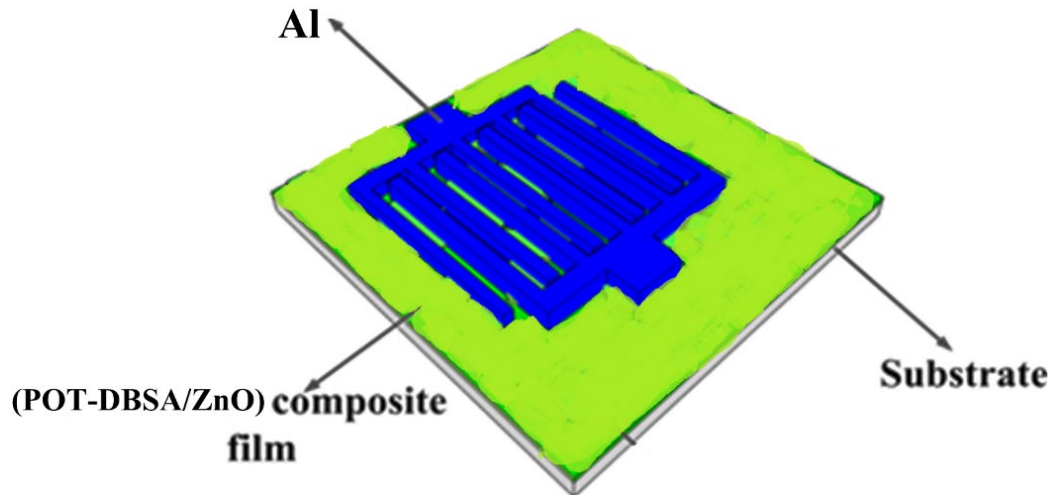


Figure 1: Schematic illustration of the electrical conductivity based on Nanoparticle POT-DBSA and composite on Al substrates.

3. Results and Discussion

3.1. FESEM and EDX analysis

FESEM images of a surface for the doping POT and dopant POT with several weight ratios of ZnO films have been shown in Fig.2 (a) and Fig.2 (b, c & d). The pristine POT-DBSA displays irregular morphology, shapeless agglomerates that the formation of an inhomogeneous, amorphous film, shown in Fig. 2(a). The morphology of POT-DBSA has changed by the introduction of ZnO nanoparticles, as depicted in Fig.2(b–d). Moreover, the morphology of the POT-DBSA/ZnO nanocomposite with varying weight percent ratio of ZnO nanoparticles, shows that there is no agglomeration and uniform distribution of the ZnO nanoparticles in the POT-DBSA chains. It can be seen that the size grain of ZnO encapsulated with POT-DBSA, for POT-DBSA/ 5% ZnO particle size is (37.41) nm, reduced with increasing ZnO nanoparticles content for POT-DBSA/ 15% ZnO particle size (15.45) nm), due to the possibility of agglomeration of ZnO particles, and dopant POT have declined. The EDX spectrum, Table 1 reveals the presence particle of Zn in POT-DBSA composites result from the interaction of ZnO with dopant POT, given it is absent in pure the POT-DBSA.

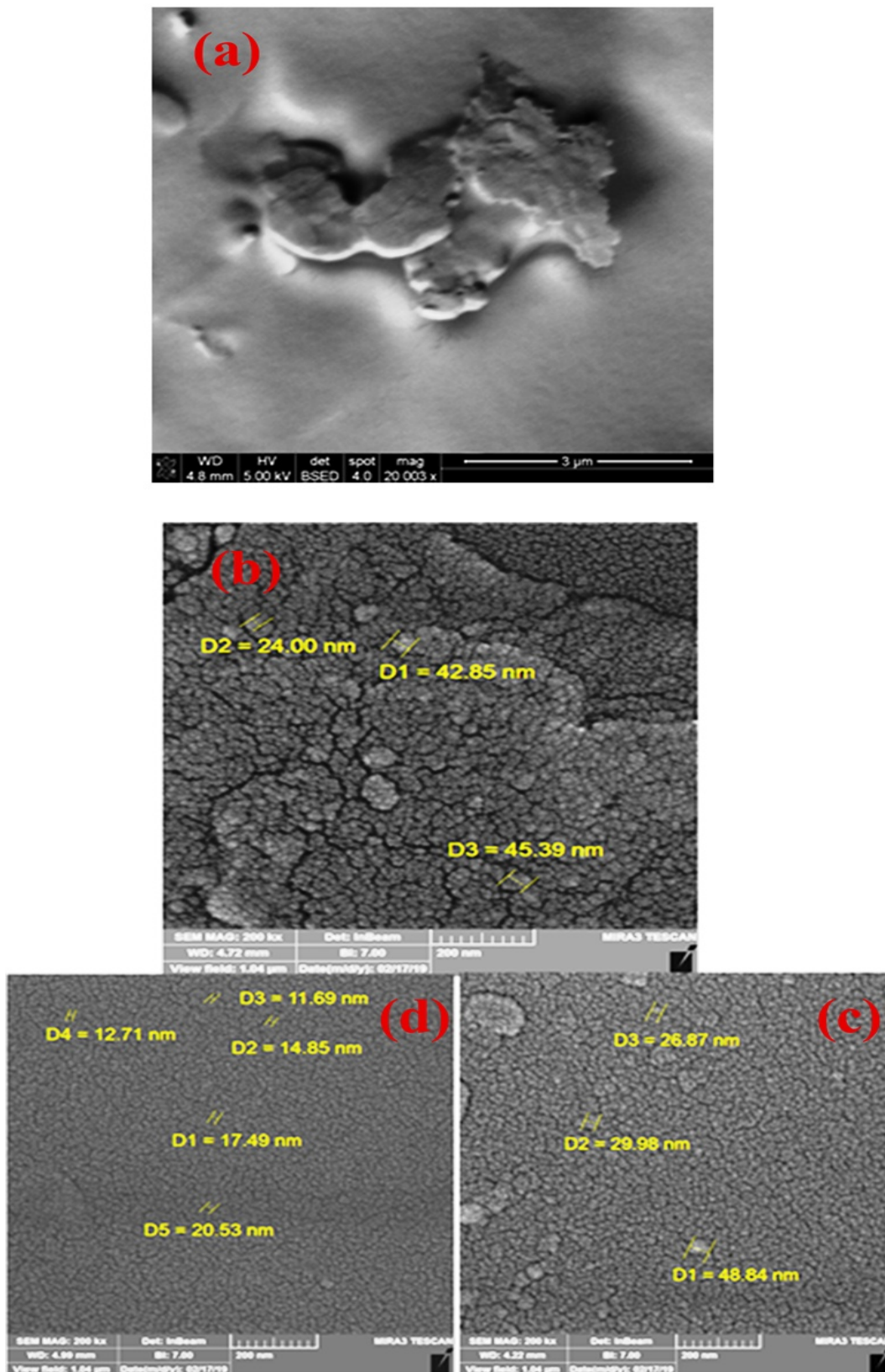


Figure 2: FESEM images of (a) POT-DBSA, (b) POT-DBSA/0.05 ZnO, (c) POT-DBSA/0.1 ZnO, and (d) POT-DBSA/0.15 ZnO.

Table 1: EDX of the POT-DBSA and POT-DBSA/ZnO nanocomposites.

Elements	Ratio of ZnO	Atomic %	Weight %
C	0%	72.4	70.4
O		18.6	24.2
S		3.2	8.4
Zn		-----	-----
Elements	Ratio of ZnO	Atomic %	Weight %
C	0.05%	75.4	62.0
O		16.2	17.7
S		6.6	14.5
Zn		0.86	3.8
Elements	Ratio of ZnO	Atomic %	Weight %
C	0.1%	74.1	60.4
O		17.6	19.1
S		7.05	15.3
Zn		0.91	4.05
Elements	Ratio of ZnO	Atomic %	Weight %
C	0.15%	56.5	44.5
O		33.9	35.5
S		6.18	12.9
Zn		0.24	1.04

3.2. XRD analysis

XRD analysis was used to examine the structure of POT-DBSA and the POT-DBSA/ZnO nanocomposites and investigate the effect of the different weights of ZnO nanoparticles on the POT-DBSA structure. From Fig.3(a) it is apparent the characteristic peaks of the POT-DBSA were found in $2\theta=19.3$ corresponding to (0 1 1) crystal planes of POT. In the presence of ZnO in dopant polymer, it can be seen that the XRD patterns of composites in Fig .3 (b, c, and d) are similar to that of the POT-DBSA. This is due to the less content of ZnO particles in polymer, it has no effect in diffraction patterns of POT-DBSA. The intensity of peaks was increased as the amount of ZnO nanoparticles increased in POT-DBSA, which means that there is a physical interaction of ZnO particles with POT-DBSA[27].

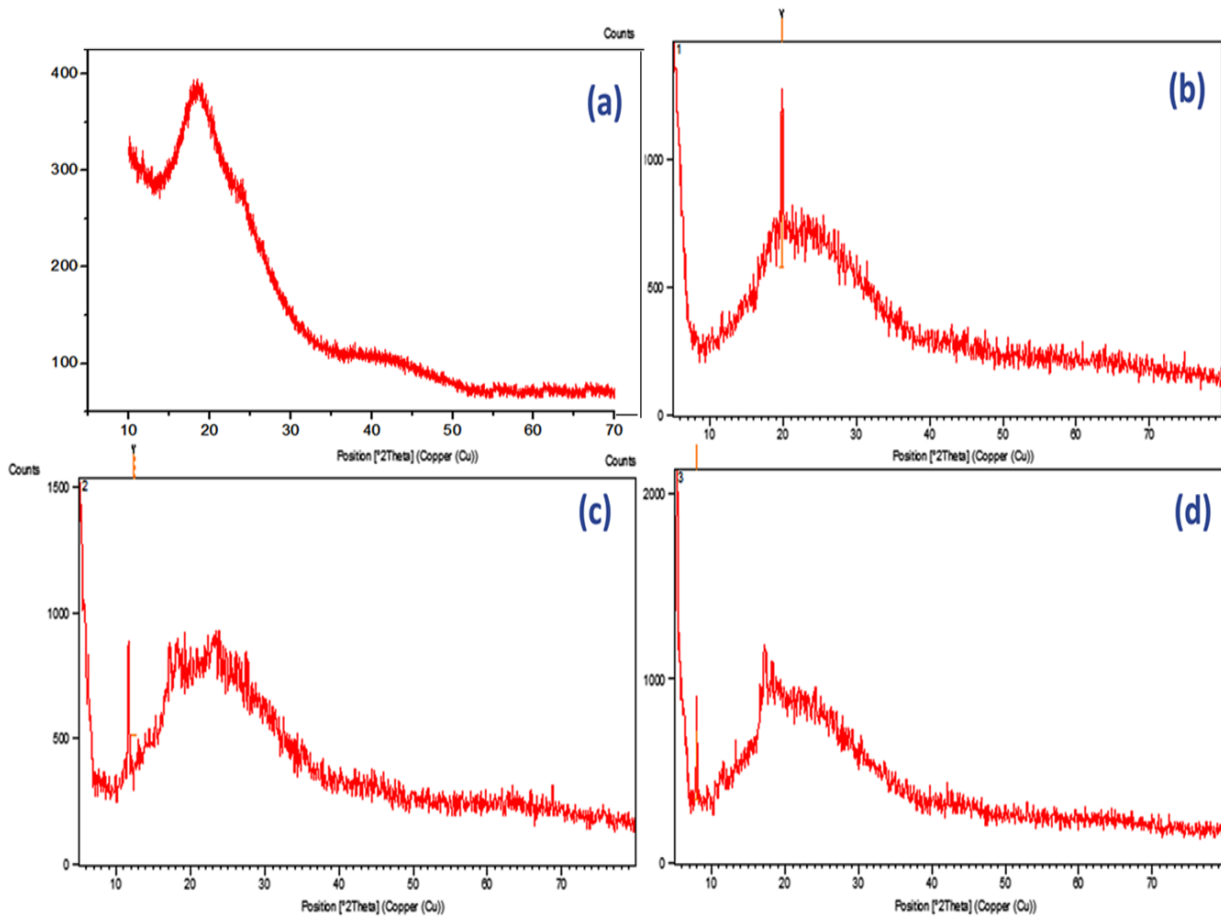


Figure 3: XRD patterns of (a) POT-DBSA, (b) POT-DBSA/0.05 ZnO, (c) POT-DBSA/0.1 ZnO, and (d) POT-DBSA/0.15 ZnO nanocomposites.

3.3. Electrical Properties

Table 2 gives the values of conductivity of dopant POT and POT-DBSA/ 0.05,0.1,0.15 ZnO at room temperature which were measured using digital finger technique and films were deposited on a glass slide. The sequence of conductivity is found to be as POT-DBSA < POT-DBSA/ 0.05 ZnO < POT-DBSA/0.1 ZnO < POT-DBSA/0.15 ZnO. Among the different weight percentage of ZnO in POT used for the composite purpose, 15wt% ZnO composites POT shows higher conductivity. The increase in conductivity when increasing the amount of ZnO could be due to the increase of efficiency of charge transfer by a contribution of π -Polaron and Polaron bands shaped in the bandgap of the composite between ZnO and POT chains[28]. The I-V curves as shown in fig. 4, of POT-DBSA and POT-DBSA/ZnO nanocomposites shows apparently rectifying behavior indicating the formation of a diode between the hybrid POT–ZnO nanocomposites with aluminium (Al). The reason goes back to probably due to the presence of surface states in POT-ZnO and defects at the film interface[29]. The current continuously increased with applied voltage. Further, we can see that as the weight ratio of ZnO in POT increases then the current in I-V curves is also increased therefore these curves indicated that the highest values of current at the higher concentration of ZnO.

Table 2: The electrical conductivity of POT-DBSA and composites.

Sample	σ (S.cm ⁻¹)
(a) POT-DBSA/0% ZnO	1.9×10^{-7}
(b) POT-DBSA/5% ZnO	1.3×10^{-6}
(c) POT-DBSA/10% ZnO	3.1×10^{-6}
(d) POT-DBSA/15% ZnO	1.0×10^{-5}

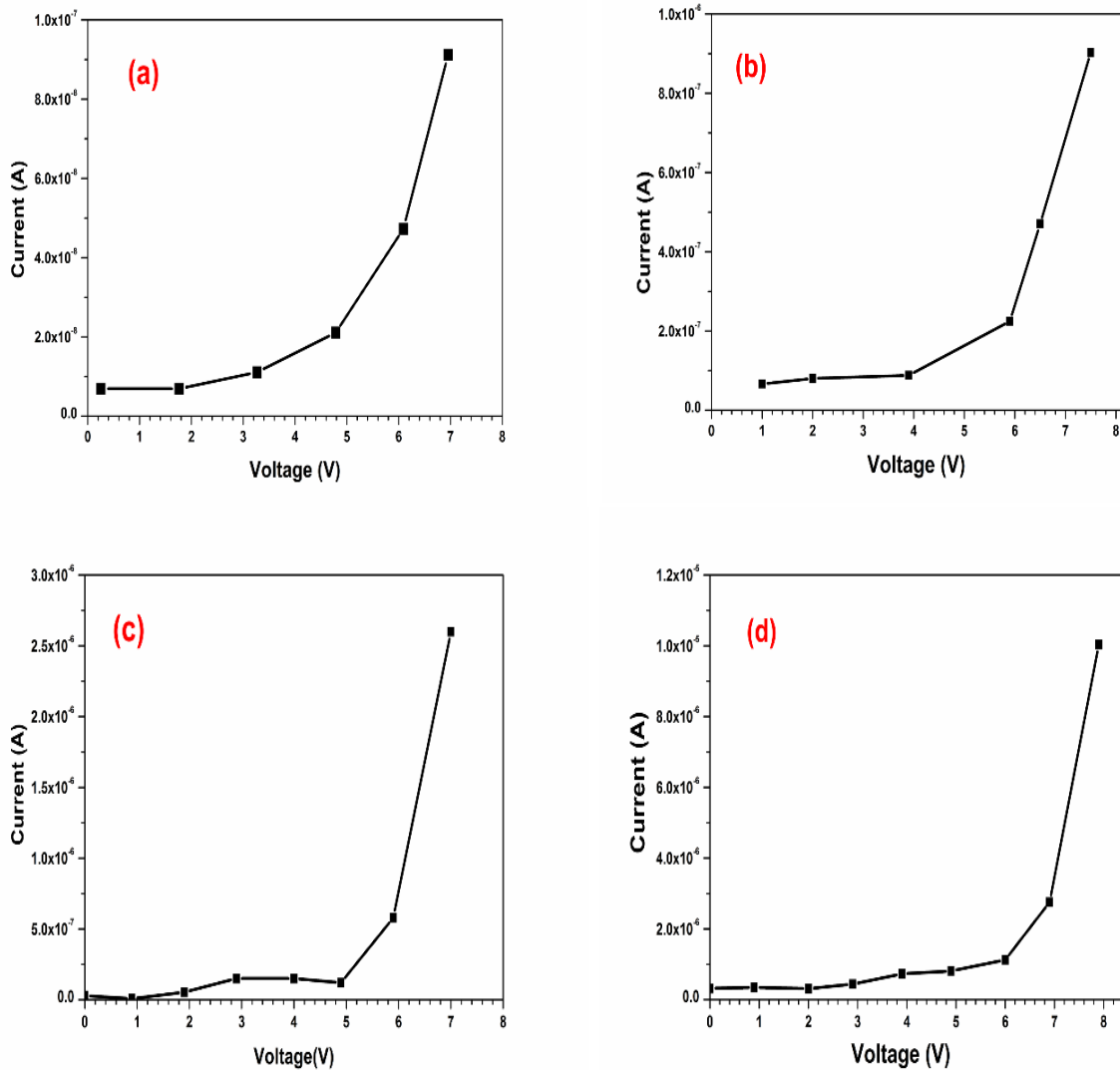


Figure 4: I-V characterization of (a) POT-DBSA, (b) POT-DBSA/0.05 ZnO, (c) POT-DBSA/0.1 ZnO, and (d) POT-DBSA/0.15 ZnO nanocomposites.

Conclusion

POT doping with DBSA/ ZnO nanoparticles (the weight ratios POT/ZnO: 1/5%, 1/10%, 1/15%), was successfully fabricated via in-situ polymerization of OT monomer and ZnO particles. FESEM analysis revealed the pristine POT-DBSA displays irregular morphology, shapeless agglomerates that the formation of an inhomogeneous film. The morphology of it has changed to agglomeration and uniform distribution film by the introduction of varying weight percent ratio of ZnO nanoparticles in the POT-DBSA chains. XRD analysis revealed the intensity of the peaks was raised as the amount of ZnO nanoparticles increased in POT-DBSA. I-V characteristics of all ratios show rectifying behavior with electrical conductivity increase as the ZnO amount increases from 1.9×10^{-7} at 0% to 1.0×10^{-5} at 20%.

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