Fabrication Of Poly (O-Toluidine) (POT) For DC Conductivity And Schottky Diodes Application By Sandwiching Nano Zno As An Interfacial Region By In Situ Polymerization Technique

Praveen Hari (praveennano123@gmail.com)
Nehru College of engineering and research centre https://orcid.org/0000-0002-3945-2122
Thushara K M
Nehru College of engineering and research centre

Research Article

Keywords: Barrier properties, Diode application, Metal-polymer complexes and Poly (o-toluidine)

Posted Date: March 3rd, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1406654/v1

Fabrication of Poly (o-toluidine) (POT) for DC Conductivity and Schottky Diodes application by sandwiching nano ZnO as an interfacial region by *In situ* polymerization technique

Praveen.H[1], Tushara.K.M[2]

[1, 2] Nehru College of engineering and research centre, Pampady, Thiruvilwamala, Kerala 680597, India

Corresponding author: Praveen.H, praveennano123@gmail.com

Abstract

The influence of nano ZnO in Poly (O-toluidine) for Schottky diode application was prepared by *in situ* chemical polymerization method with different weight perctange of nano zinc oxide. FTIR results reveals that the amorphous nature has been faded due to the addition of nano zinc oxide and thus it was effective for crystallinity. SEM images proves that the uniformity arrangement of particles in spherical shape and the composition of particles in the POT-n-ZnO is proved from the EDAX analysis The current increase inside the sample increases due to the external source of light, electrical conductivity inside the sample has enhanced due to increase in Zinc oxide (nano) concentration. DC Conductivity of the prepared samples was high and POT doped with 75wt% of nano ZnO shows highly appropriateness material as direct current conducting substance. The results of this work disclose that the material is appropriate for diode due to increase in barrier height and ideality factor and another factor was forward bias current enhances in all the samples while reverse biased current was fade. Scope of this work was to fabricate the diode and conducting material with cost effective, high yield and vastly efficient material.

Key words: Barrier properties, Diode application, Metal-polymer complexes and Poly (o-toluidine).

1. Introduction

Conducting polymer has played vital role in electrical industry due to its specifications in conductivity nature and many researches has reported that conducting polymer enhances its conductivity property by increasing the dopant like metal oxides due to interfacial interaction between polymer and metal oxide leads to free electrons to move more rapidly[1]. The use of transistors and diodes has more significance due to its importance in electronics equipments where the natural resources are peter out with daily use thus the use of electrical components has raised, electric vehicles is one of the example due to a reduced amount of production of petroleum. The collaboration of conducting polymers in electronic industries like LED and diode has significant importance due to their excellent electrochemical and optical properties [2]. Another important factor for the conducting polymers is the presence of conjugated bonds where it depends on the method of synthesizing the material [3]. The application of conducting polymers for diode applications like polyaniline, polyacetylene...etc has been investigated by many authors [4-6]. Some of the parameters for diode applications are ideality factor, rectifying ration, work function and barrier height, the nature of dopant affects the Fermi level of the sample. Polyaniline and its derivates are intrinsic conducting polymers but Poly (O-toluidine) doped with zinc oxide has not been investigated by any of the researchers. The polymer doped with metal oxide is suitable for diode application and some of the research has done on it like poly (p-phenylene vinylene) by T.P Nguyen et.al, but for Schottky diode it has very less number of researches due to non suitability of the polymer for Schottky diode application. But in our research work we synthesized POT-n-ZnO with suitable catalyst as potassium dichromate for the rapid chemical reaction. The prepared sample is named as by prefix Poly (o-toluidine) (POT) and weight perctange of nano ZnO doped, 25wt% of nano ZnO doped with POT is named as PZnO25, vice versa PZnO50 and PZnO75 respectively. In Current voltage relationship (diode) of the prepared samples is named as Z1, Z2 and Z3 for PZnO25, PZnO50 and PZNo75 respectively.

The aim of our present work is to fabricate the Poly (O-toluidine) by doping nano zinc oxide for the diode application and DC conducting material in cost effective by choosing *in – situ* polymerization technique. The results of these samples are well concurrent and more advanced in results with the other samples of same nature.

2 **Experimental procedures**

POT is prepared by doping nano zinc oxide where the entire chemicals were purchased from Sigma - Aldrich. Initially O-toluidine (OT) (monomer) of 5ml is added to the potassium dichromate (5mg) and kept under stirring for one hour. Dilute HCL of 2.36ml is added to the nano zinc oxide powder and kept for stirring as like OT solution and the both solutions mixed together and kept in stirring for 12hours. The mixture solution is washed in ethanol and purified to keep in hot air oven for 8hours thus finally obtained material is made into fine powder. Same procedure is repeated for different weight perctange of zinc oxide with different amount (mg) of zinc oxide.

3 Result and discussion:

3.1 Fourier Transform Infrared Characterization (FTIR)

FT-IR spectrometer (Make: Model: Nicolet iS50 Make Thermo Fisher Scientific, Spectral Range: 7800 – 350 cm^{-1} in MID IR and up to 100 cm^{-1} in FAR IR, Spectral Resolution 0.09cm^{-1}, Signal to noise ratio 55,000:1) was used to study functional groups in prepared samples. Fig.1 shows the FTIR spectra of POT- n-ZnO. The spectra reveal that incorporated additive element (n-ZnO) makes substantial variation in structure of composite sample and absorption band increases with high concentration of n-ZnO. Peaks of 2θ observed in between 3000 – 3410cm^{-1} is due to the N-H stretching vibrations and 2θ observed between 500-650cm^{-1} is due to the metal oxygen stretching vibrations [7-12],quinoid rings of C-N stretching is observed at peaks of 2θ value at 1498cm^{-1}, peaks observed 2θ value at 1600cm^{-1} is due to benzenoid ring of C-N stretching, the peaks of 2θ value at 1247cm^{-1} is due to the C-N stretching mode of benzenoid ring [12], peaks of 2θ between at 3400-3500cm^{-1} is due to N-H stretching vibration [9].Peaks of 2θ at 1593,1496,1155 and 814cm^{-1} indicates the presence of POT in the composites [9,10].And these peaks are shifted to the lower wave number 1497.21cm^{-1} is due to the shift of the characteristics absorption peaks, which may be attributed to the formation of hydrogen bonding between ZnO and the n-H group of POT on the surface of the nano ZnO particles

3.2 X-ray diffraction (XRD)

XRD analysis was analyzed by advance diffractometer with monochromatic CuKα radiation (λ = 3.54A^{O}), Bruker D8 Advance Twin- Twin. Fig 2 Displays X-ray diffraction pattern of POT-n-ZnO and it reveals that the POT doped with 25wt% of ZnO has more amorphous nature that the other two samples. Polyaniline doped with the Y_2O_3 was investigated for temperature depended and electrical conductivity by Mohammed Saeed et.al [11] and the results of XRD reveals that the pure polyaniline has high amorphous nature and the same doped with the Y_2O_3 enhances the crystalline nature thus the same factor effects in our present work. The previous works also reveals that the method of synthesizing the polymer affects the crystallinity [12]. PZnO25 exhibits only one peak at 30.85° and it is due to the amorphous nature FTIR graph also supports with the same statement. PZnO50 has peaks at 28.75°, and 32.25° which show that it is amorphous in nature but partially crystalline where 32.25° is a crystalline peak. PZnO75 has peaks at 28.65°, 36.14°, 41.34° and 43.57°

corresponds to (002), (101), (102) and (200) (JCPDS No. 89-1397 and 36-1451) the nature of peaks where sharp (FTIR graphs proves this statement where the peaks are sharp at 814cm^{-1} is due to the strong interaction between POT and nano ZnO) thus it is reveals that the crystallinity nature of the sample enhances due to incorporation of the dopant, the number of peaks are added comparing with the previous two samples for PZnO75 [11,12] and the crystalline size of the prepared sample is tabulated in table 1. The size of the prepared samples were calculated by using Scherrer equation as follows

$$D = \frac{k\lambda}{\beta cos\theta} \text{-----------------------------------} \qquad (1)$$

where, D is the crystallite size, k is the shape factor for the average crystallite (0.9), λ is the wavelength of the X-ray which is 1.54 Å for Cu target, β is the full width at half maxima of the crystalline peak in radians, θ is the angle between incident and reflected rays

3.3 Scanning electron microscope (SEM) & Energy Dispersive X-ray spectroscopy (EDAX)

SEM-EDAX: Jeol 6390LA/ OXFORD XMX N, Accelerating voltage: 0.5 to 30 kV, Filament: Tungsten, Magnification x 300000, EDAX resolution 136 eV, EDAX detector area 30 mm^2 was used to examine the morphological and elements composition of the prepared sample. SEM images and EDAX spectrum of PZnO25 is shown in Fig.3 (a), it reveals that particles are almost spherical and bigger grains owing to the amorphous nature of the polymer and from EDAX spectrum it was evident that ZnO is present with POT structure, the ratios of zinc, oxygen is 0.64 at% and 20.38 at% remaining for POT [13]. The SEM images and EDAX spectrum of POT doped with ZnO at 50 wt % exposed in Fig 3(b), grains are smaller and spherical shape. From EDAX spectrum it is clear that by doping ZnO with 50 wt% its concentration increases in POT-ZnO nanocomposites. The atomic ratios of Zinc and oxygen are 5.15at% and 67.05at% respectively. By comparing with POT-ZnO of 25wt% the amount of ZnO is increased in this composite [14, 15]. Fig.3 (c) shows the SEM images and EDAX spectrum of POT doped with ZnO at 75 wt %, the morphology is altered due to increase in concentration of ZnO in POT and agglomeration of Zinc oxide, POT has declined. The atomic ratios of Zn and oxygen are at 1% and 74at% respectively and the prepared sample (POT-n-ZnO) shows improved capacitance due to increase in atomic ratio of oxygen.

3.4 Electrical conductivity (DC)

POT derivate of PANI is low cost and desirable material for electronics applications; R.A. Nafdey et.al reported by doping gold and $FeCl_3$ in polyaniline but it leads to costly due to addition of gold where it can't be affordable for industries to produce large extent of production[16-18].The application of electronic appliances is significant for the technologies. The process of movement of weakly bonded particles under thermal influence takes place due to applied electrical field is the electrical conductivity of the material and it depends on the factors like nature of material doped, concentration of material doped, applied electrical field and applied temperature. In present work the DC electrical conductivity measurement of PZnO25, PZnO50 and PZnO75 was analyzed using 4 – in – line probe process.

The previous work of Abdul Shakoor et.al [19] investigated about electrical conductivity of PANI doped with Montmorillonite (MMT) shows the maximum DC conductivity at 0.25 S/cm that was very low owing to the insulating layers in the interfacial region, which makes partially movement of electrons but only at high temperature thus it does not found more suitability in DC conductivity. In our present work, DC results reveals that the conductivity of the prepared samples have enhanced in two different types, like increasing temperature enhances the conductivity within the material and other method of increasing the conductivity was by increasing the weight perctange of the dopant. PZnO25 has an electrical conductivity ranges from 2.8 x 10^{-5} S / cm to 4.8 x 10^{-5} S / cm. with a temperature ranges from room temperature to 120°C and for PZnO50 it has a range from 3.3 x 10^{-5} S / cm to 4.10 x 10^{-5} S / cm with the same temperature range. The conductivity ranges for PZnO75 is 4.53 x 10^{-5} S / cm to 9.33 x 10^{-5} S / cm which is more than the twice comparing with the other two samples. Figure 4 (a-c) shows the graphical illustration of conductivity (prepared samples). The conductivity for the prepared samples is measured by the equation as follows

$$\boldsymbol{\sigma = (\rho) \quad x \quad \frac{d}{A}} \text{ --------------------------- } \mathbf{(4)}$$

Where 'ρ' is the resistivity of the samples, 'd' is the inter probe distance, and 'A; is the cross sectional area of the samples.

The raise in conductivity with the increase in doping weight perctange is due to transformation of charges together with the control of Fermi level. Doping of ZnO (nano) leads to interrelate the π – conjugated structure of the POT and another factor is interfacial interaction and it increases due to increase in doping weight perctange of ZnO [19]. Raise in temperature leads to enhance the conductivity of the prepared sample and it is due to the thermal excitation of electrons in the POT-n-ZnO nano composites. Table 2 shows the conductivity of the prepared sample (at different temperature). SEM and FTIR results reveal that the prepared samples crystallinity enhances thus it supports for the DC conductivity analysis [20]. Fig 4 (a-c) predicts the Electrical Conductivity (DC) of prepared samples The free particles gain more kinetic energy and cross the band gap due to the influence of temperature which makes the prepared sample more conductivity, the another important factor is ionic conduction also enhances in the POT due to the addition of Zinc Oxide and high concentration of ZnO in the POT structure has more ionic nature that facilitate for the high conductivity

3.5 Current voltage characteristics of POT doped with nano ZnO at different weight perctange

Fig 5(a-c) shows current voltage relation in dark and light of PZNo25, PZNo50 and PZNo75 as Z1, Z2 and Z3, it is evident that the prepared samples have good rectifying performance that is the indispensable part of Schottky performance and the other important result from the graph is that exponentially amplify in forward bias current and feeble increase in reverse bias current shows good rectifying property for the Schottky diode nature. The light generated current due to the incident of light enhances with respect to bias voltage. The lowest ideality factor was found for POT doped with 75wt% of nano ZnO. Tunnelling current in the interfacial region and electron – hole pair is also an motivation for the better performance of ideality factor and light generated current [21]. Table 3 shows the conductivity of the prepared samples. The current conduction mechanism of the diodes was explained by the thermionic emission theory (TE) as follows

$$\mathbf{I = I_0 \exp\left(\frac{qV}{nKT} - 1\right)} \text{---------- } \mathbf{(1)}$$

where 'I_o'- reverse saturation current, 'q' - electron charge, 'V' - applied voltage, 'n' - ideality factor, 'K' - Boltzmann constant and 'T' - absolute temperature.

The ideality factor of the diode is determined from the slope and the intercept of the semi-log forward bias of J-V plot for $V \geq 3kT/q$ using

$$\mathbf{n = \frac{q}{KT}\frac{dV}{d(\ln J)}} \text{ ------- } \mathbf{(2)}$$

The Φ_b and n are calculated using the following relations

$$\Phi_b = \frac{KT}{q} \ln\left(\frac{A^* T^2}{I_0}\right) \quad \text{--- (3)}$$

Where A^* - Richardson constant.

The relationship between anti log of current charge density and voltage of PZNo25, PZNo50 and PZNo75 as Z1, Z2 and **Z3 is** exposed in Fig 6 (a-c) and it reveals that the barrier height increases due to increase in dopant (ZnO) [22, 23]. The oxygen vaccines make the polymer structure more conductive by the movement of carriers with sufficient energy, it has important role for diodes (photosensitivity). The photo electric advantage of the prepared samples results in optical light harvesting process that enhances the nature of diode. From the results of Current and voltage characteristics of the prepared ample it is observed that the material is suitable for Schottky diode.

4. Conclusion

An *In situ* polymerization process of synthesizing POT doped with different weight perctange of nano ZnO. The FTIR and EDAX results conforms the presence of sample mixture, SEM images shows that uniform granular size of the prepared sample. POT doped with 75wt% of the nano ZnO has highest conductivity comparing with the other two samples due to free movement of electrons by the application of temperature. Interfacial region of ZnO and POT makes the transparent medium for the electrons motion. Prepared samples are suitable for Schottky diode due to the parameters like ideality factor, barrier height and reverse saturation current among the prepared sample POT doped with 50wt% of nano ZnO has highly suitable for Schottky diode application, have high current sensitivity due to the light which is induced on the sample.

5 Abbreviations

DC Conductivity (Direct current conductivity), EDAX (Energy Dispersive X-ray spectroscopy), FTIR (Fourier Transform Infrared Characterization), HCl (Hydrochloric acid), OT (ortho toluidine), POT (Poly (o-toluidine)), PZnO25 (POT ZnO 25wt %), PZnO50 (POT ZnO 50wt %) and PZnO75 (POT ZnO 75wt %), SEM (Scanning electron microscope), Wt% (weight perctange),

Conflict of Interest: The Authors (Dr.Praveen.H and Thushara.K.M.) declare that we have no conflict of interest.

6. **References:**

1. Lijun Fua , Qunting Qub , Rudolf Holzea,c,d*, Veniamin V. Kondratievd , and Yuping Wua, Composites of metal oxides and intrinsically conducting polymers as supercapacitors electrode materials: The best of both worlds?, Journal of materials chemistry A, DOI: 10.1039/x0xx00000x
2. G.Inzelt, Recent advances in the field of conducting polymers, J. Solid State Electrochem.21 (2017), doi: 10.1007/s10008-017-3611-6.
3. Sh. M. Ebrahim, A. Gad, A. Morsy, Highly crystalline and soluble dodecylbenzene sulfonic acid doped poly(o-toluidine), Synthetic Metals 160 (2010) 2658–2663, doi:10.1016/j.synthmet.2010.10.021
4. S. Carrara, V. Bavastrello, M.K. Ram, C. Nicolini, Thin Solid Films 510 (2006) 229–234.
5. Li-M. Huang, T.ChenWen,A. Gopalan, F.Ren, Mater. Sci. Eng. B104 (2003) 88–95.
6. R.K. Gupta, R.A. Singh, Comp. Sci. Technol. 65 (2005) 677–681
7. M. T. Ramesan, P. Jayakrishnan, Role of Nickel Oxide Nanoparticles on Magnetic, Thermal and Temperature Dependent Electrical Conductivity of Novel Poly (vinyl cinnamate) Based Nanocomposites: Applicability of Different Conductivity Models, J Inorg Organomet Polym, 6, (2016)
8. Chuanbo Hu, Ying Li, Yazhou Kong, Yushi Ding, Preparation of poly(o-toluidine)/nano ZnO/epoxy composite coating and evaluation of its corrosion resistance properties, Synthetic Metals, 214, (2016).
9. Syed Ashfaq Nabi, Rani Bushra, Mu. Naushad, Amjad Mumtaz Khan, Synthesis, characterization and analytical applications of a new composite cation exchange

material poly-o-toluidine stannic molybdate for the separation of toxic metal ions, Chemical Engineering Journal, 165, (2010).

10. PriteePawar, A.B. Gaikwad, P.P. Patil, Corrosion protection aspects of electrochemically synthesized poly(*o*-anisidine-*co*-*o*-toluidine) coatings on copper, Electrochimica Acta, 52, (2007).
11. Muhammad Saeed, Abdul Shakoor, and Ejaz Ahmad, Temperature Dependent Electrical Conductivity of Polyaniline/Y2O3 Composites, Polymer Science, Ser. A, 2013, Vol. 55, No. 9, pp. 549–555.
12. S. Saravanan, C. J. Mathai, A. R. Anantharaman,S. Venkatachalam, and P. V. Prabhakaran, J. Phys.Chem. Solids **67**, 1496 (2006)
13. Kalpana Handore, Dipak Walunj, Prakash Chhattise, Aniruddha Chabukswar,
14. Kakasaheb Mohite, Sabrina Dallavalle, Bahule Bharat & Vasant Chabukswar, Ultrasound Synthesis of Polyindole–TiO2 Nanocomposite and Evaluation of Antibacterial Activity, 6 (2017).
15. ShehnaFarooq,Anwar-ul-Haq Ali Shah, Salma Bilal, Some insights into the structure and morphology of surfactant-doped poly(o- toluidine), *Adv Polym Technol.* (2018)
16. Aisha Batool, Farah Kanwal, Muhammad Imran,Tahir Jamil, Saadat Anwar Siddiqi, Synthesis of polypyrrole/zinc oxide composites and study of their structural, thermal and electrical properties.
17. Khwaja Salahuddin Siddiqi, Aziz ur Rahman, Tajuddinand AzamalHusen, Properties of Zinc Oxide Nanoparticles and Their Activity Against Microbes, Nanoscale Research Letters (2018) 13:141, doi.org/10.1186/s11671-018-2532-3
18. A. Elmansouri, A. Outzourhit , A. Lachkar, N. Hadik, A. Abouelaoualim, M.E. Achour, A. Oueriagli, E.L. Ameziane, Influence of the counter ion on the properties of poly(o-toluidine) thin films and their Schottky diodes, Synthetic Metals 159 (2009) 292–297
19. Abdul Shakoora, Tasneem Zahra Rizvib, and Ahmad Nawaz Sangrab, Polyanilme_Montmorilltonite(PANl_MMT)Nanocomposites:Mechanochemical Synthesis, Structure, Thermo stability and Electrical Properties, Polymer Science, Ser. A, 2010, Vol. 52, No. 10, pp. 1034–1043.
20. Y.badali, A. Nikaravan, S. Altindal, I . Uslu, J. Electron matter. 47 (7), 3510 (2018).
21. Praveen K.Jain, Deepika, K.S.Rathore, N.S.Saxena, Chalcogenide Letters 5 (2008)126-136
22. Y.badali, A. Nikaravan, S. Altindal, I . Uslu, J. Electron matter. 47 (7), 3510 (2018).

23. A. Elmansouri, A. Outzourhit , A. Lachkar, N. Hadik, A. Abouelaoualim, M.E. Achour, A. Oueriagli, E.L. Ameziane, Influence of the counter ion on the properties of poly(o-toluidine) thin films and their Schottky diodes, Synthetic Metals 159 (2009) 292–297

Figures

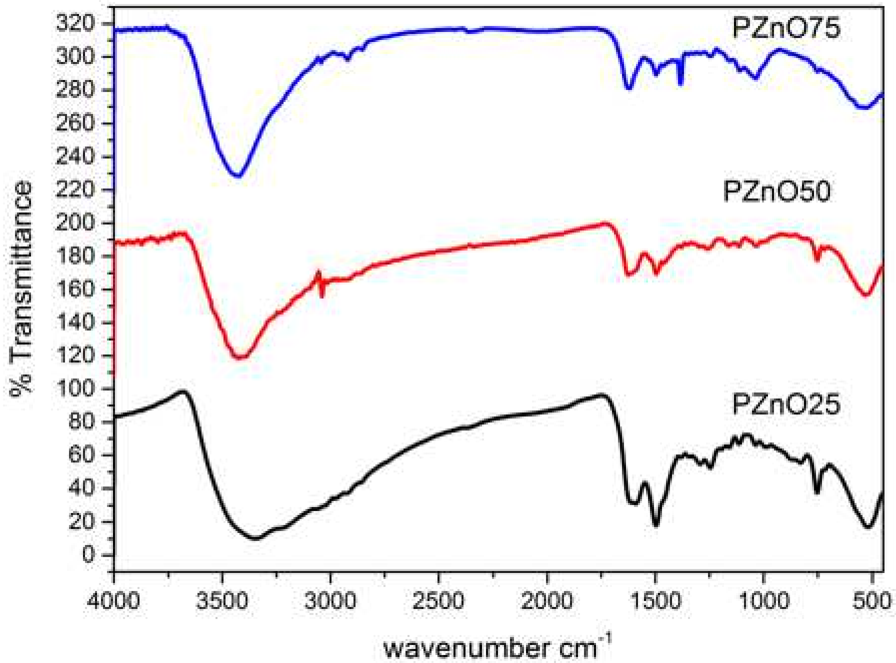

Figure 1

FTIR spectra of POT- n-ZnO

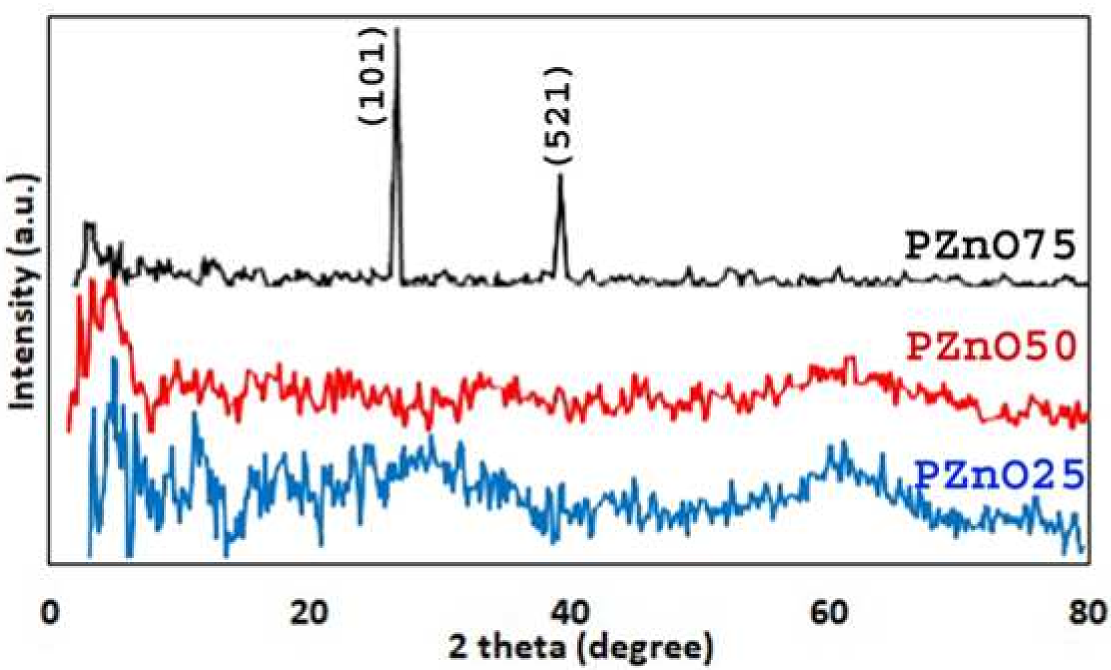

Figure 2

X-ray diffraction pattern of POT-n-ZnO

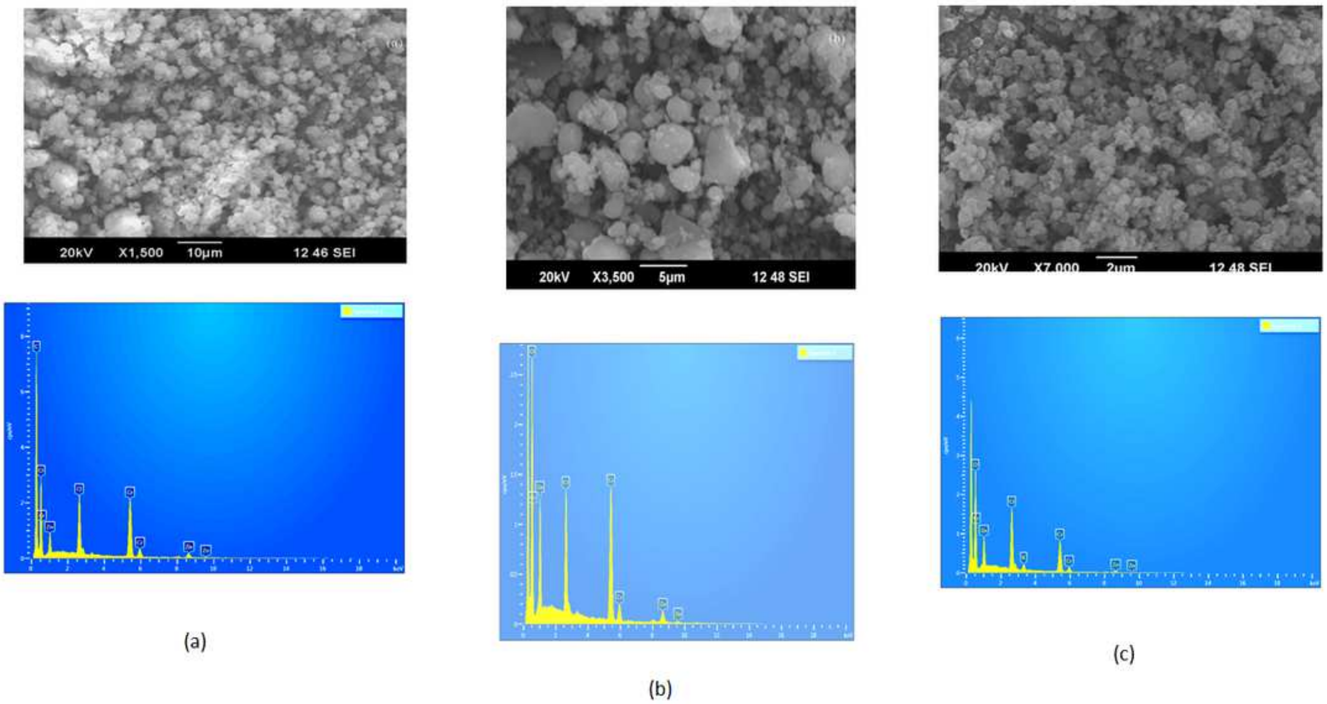

Figure 3

(a) SEM and EDAX images of PZNo25

(b) SEM and EDAX images of PZNo50

(c) SEM and EDAX images of PZNo75

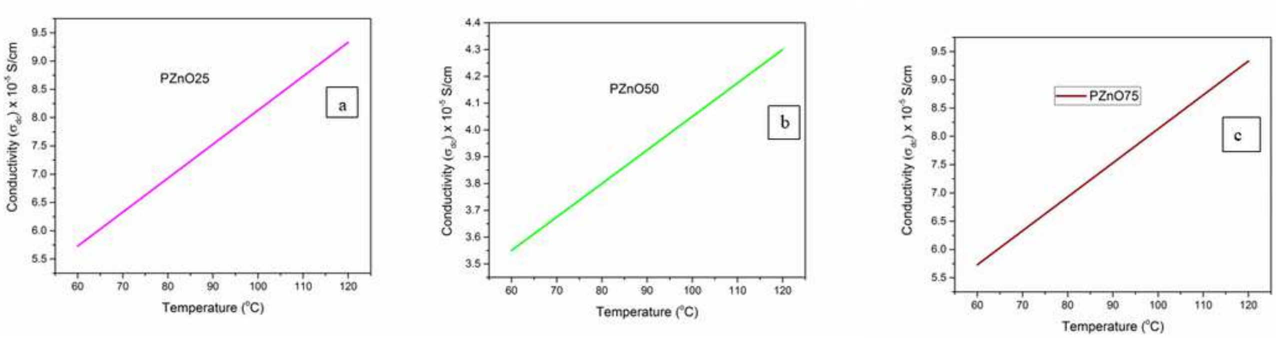

Figure 4

(a-c) shows Electrical Conductivity (DC) of prepared samples

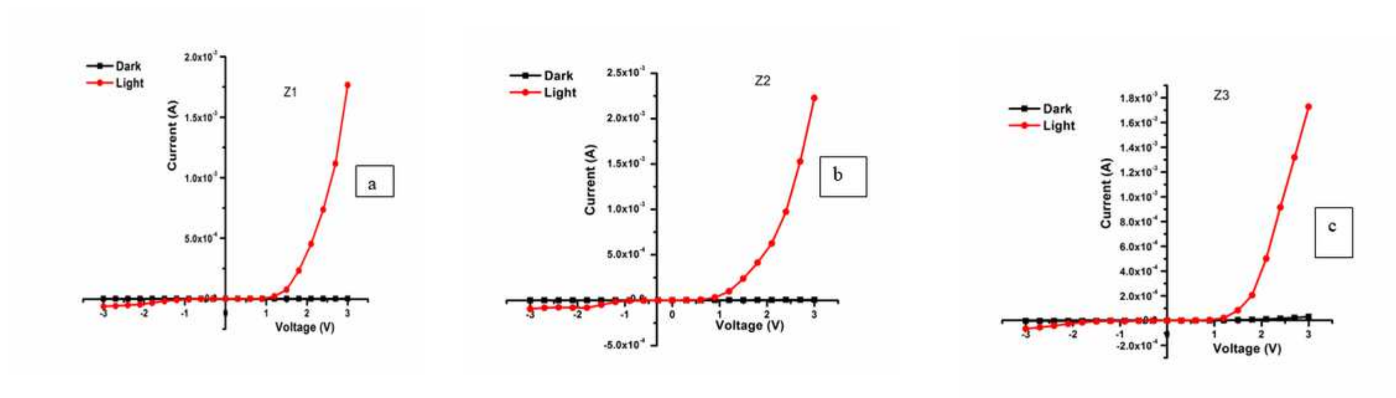

Figure 5

(a-c) Current voltage relation in dark and light of PZNo25, PZNo50 and PZNo75 as Z1, Z2 and Z3

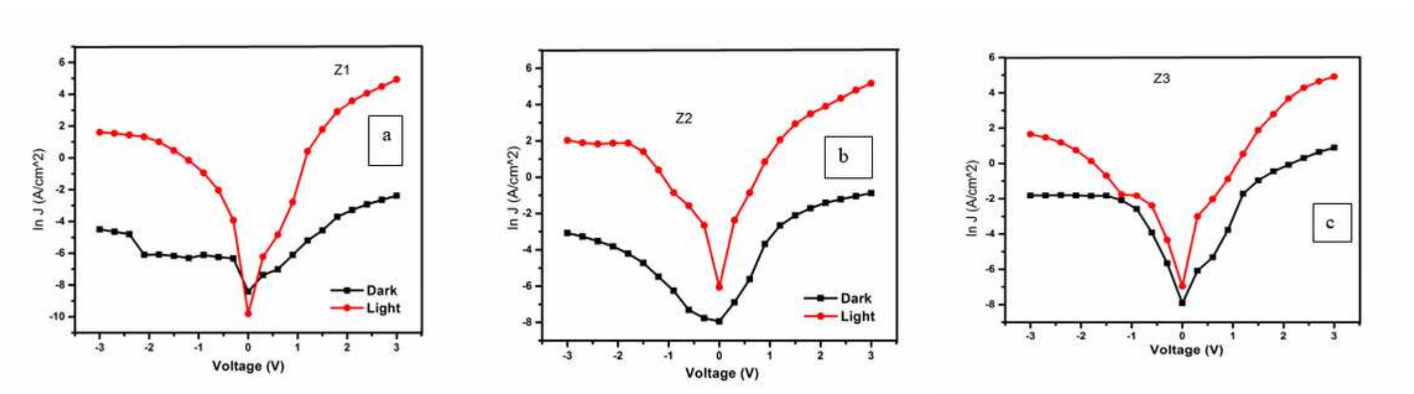

Figure 6

(a-c) determines the relationship between anti log of current charge density and voltage of PZNo25, PZNo50 and PZNo75 as Z1, Z2 and Z3