SYNTHESIS AND CHARCATERIZATION OF POLYANILINE /ZNO DOPED COMPOSITES FOR ELECTRICAL AND SENSOR STUDIES

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Abstract

This study in sequence the synthesis of Polyaniline/ZnO-doped composites. Polyaniline/ZnO doped composites were prepared by in situ polymerization of Aniline monomer in the presence of ZnO-doped with ammonium per sulfate (APS) as oxidant. Different concentrations of ZnO (10-50 wt %) metal oxides were built-in into the Polyaniline. The obtained final product was well characterized by means of PXRD, SEM, and XRD results show the presence of ZnO particles in Polyaniline. The morphology of the obtained product shows the porous, irregular shapes and agglomerated particles which are due to large amount of gas evolution during the synthesis method, PANI/ZnO for 1000 ppm of LPG was measured. *The present study demonstrates that the prepared samples are quite useful for electrochemical storage applications*

Key Words: *Polyaniline, ZnO, AC Conductivity, DC Conductivity, Sensor studies.*

1. INTRODUCTION

In recent years alternative renewable energies obtained by solar cells have attracted much attention due to exhaustion of other conventional energy resources especially fossil based fuels and due to global warming they caused [1]. In a previous study, our group had prepared composites such as ZnO nanoparticles/Polyaniline nano fibers by use of the electro spinning technique, and we have shown that the conductivity of the resulting samples was affected both by the presence of HCl vapor and the incidence of UV illumination. However, when compared to the present results, in that study, only small quantities of very short fibers with a low UV sensitivity were obtained. Electro spinning has been recognized as a simple and efficient technique to produce polymer nano fibers after an external electric field is imposed on a polymer solution or melt. In addition, it is known that CPs can be electro spun after being mixed in carrier solutions of polyvinyl alcohol (PVA), nylon-6, poly(methyl methacrylate), or polyamide. However, the blending with an insulating binder introduces a conductivity percolation threshold that impacts, in a negative manner, the use of CPs in some applications where high conductivity values are desired. Thus the synthesis of novel conducting polymers and study of their physical properties has been of prime importance. Aqueous electrochemical process in an environmentally friendly and efficient technique used to process conducting polymer. It is widely preferred because of its simplicity and it can be used as a one-step method to form polymer. It allows efficient control of the physiochemical properties of the coatings and it can also be easily scaled up for large scale production [2-4]. Conductive polymers had been the topic of the large number of investigations during last decades because of their unique properties such as mechanical strength, electrical conductivity, corrosion, stability and possibility of both oxidative and electrochemical synthesis. Hence PANI is useful in wide area of application: such as solar energy conversion, rechargeable batteries, electro chromic displays, electrochemical sensors, capacitors and active corrosion protector [5-6]. Due to ease of synthesis, processing environmental stability and low synthetic cost, so Polyaniline is probably the most important industrial conducting polymer today [7-8]. The use of conducting polymers for photovoltaic applications has been reported [9]. Composites have become one of the most extensively studied materials all over the world, as they have shown to possess several technological applications. Further, composites composed of conducting polymers and metal oxides have opened many applications *e.g.* in drug delivery, conductive paints, rechargeable batteries, toners and smart windows *etc.* [10]. The present study especially aims to investigate PANI-ZnO composites in order to obtain a new noble material which can be utilized for

electrical applications. ZnO is a semiconducting material that has a direct wide band gap of 2.16 eV at room temperature. Indeed ZnO is a peculiar material that exhibits multiple properties that include piezoelectric, semiconducting, pyroelectric and photo catalytic activities. Liquefied Petroleum Gas (LPG) is the mixture of hydrocarbons mainly propane and butane. Accidental leakage of LPG even at low concentrations creates a serious threat to human lives and personal safety as it is a flammable gas. The Lower Explosive Limit (LEL) as specified by National Institute for Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA) standards for chemical hazards is 21,000 ppm (2.1% by volume in air) for propane and 19,000 ppm (1.9% by volume in air) for butane. Permissible Exposure Limit (PEL) for LPG as specified by NIOSH and OSHA standards is 1000 ppm. The concentration-response relationship for most gas sensors approximately exhibits either saturated linear behavior, i.e. linear for low concentrations and saturated for higher concentrations, or logarithmic behavior. LPG is primarily used as fuel for vehicles and as cooking gas for household applications. Precise monitoring of leakages of LPG even at low concentrations can be beneficial to prevent accidental explosions. Among the various conducting polymers, Polyaniline (PANI) has been investigated as a potential material for gas sensing applications, due to its controllable electrical conductivity, environmental stability and interesting redox properties associated with the chain nitrogen's. It is the unique type of conducting polymer in which the charge delocalization can, in principle, offer multiple active sites on its backbone for the adsorption and desorption of gas analytic [12].

In the present paper, PANI/ZnO composites were prepared by *in situ* polymerization of aniline monomer with different doping concentrations of ZnO. All the composites have been analyzed using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The dc conductivity of these composites was studied as a function of temperature at different dopant concentrations [11].

2. SYNTHESIS OF POLYANILINE

The synthesis Polyaniline (PANI) was based on mixing liquid solution of aniline hydrochloride and APS at 32^0c temperature, followed by taking part of Polyaniline hydrochloride by filtration and drying. An equi-molar volume of aniline and hydrochloride acid was dissolved in distilled water in a beaker to obtain 100 ml of solution. Similarly, ammonium per sulphate (0.6M) was dissolved in 100 ml water. Both solutions were left 1 hour at room temperature and then mix in a beaker, stirred with a mechanical stirrer and allowed to polymerizing. After a day, the PANI precipitate was collected on a filter washed with 0.3 M HCL and acetone repeatedly. The Polyaniline hydrochloride powder was then kept at 60^oC for 24 hours [13].

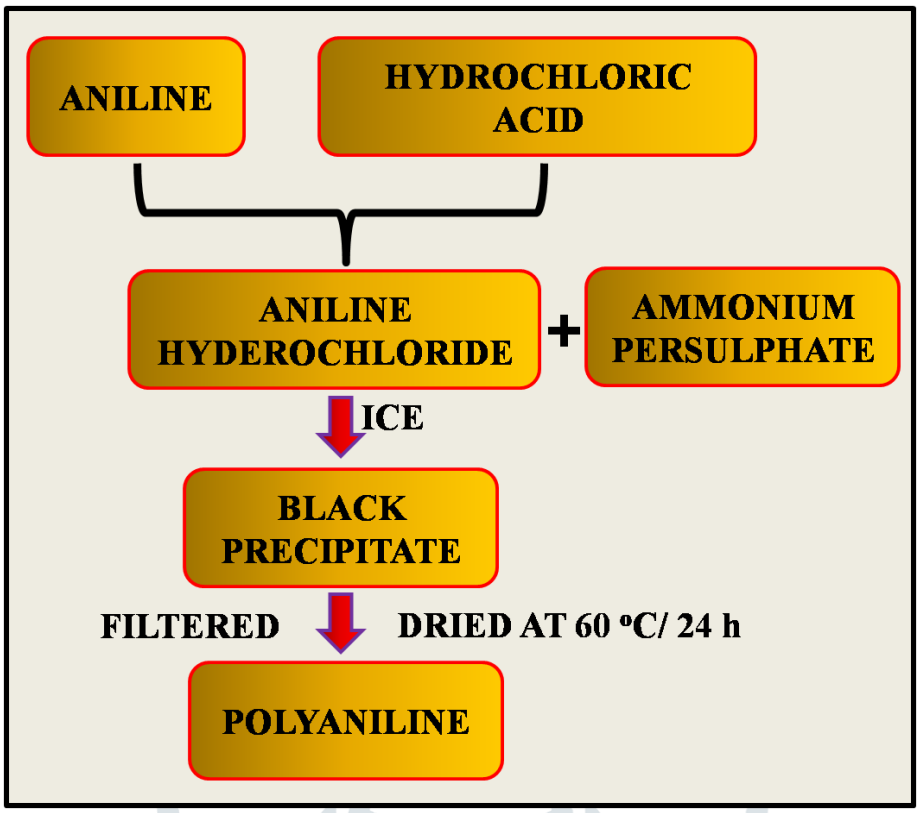

Fig.1. Flowchart for the synthesis of pure Polyaniline.

2.1 SYNTHESIS OF POLYANILINE/COPPER OXIDE COMPOSITES

Synthesis of Polyaniline–Copper oxide composites were carried out by *in-situ polymerization* method. Aniline (0.3 M) was mixed in 0.3 M HCl and stirred for 15 min to form aniline hydrochloride. Copper oxide particles were added in the mass fraction to the above solution with vigorous mixing in order to keep the Copper oxide homogeneously suspended in the solution. To this solution, 0.6 M of APS, which acts as an oxidizer was slowly added drop by drop with continuous mixing at ice temperature for 4 hours to completely polymerize. The precipitate was filtered, washed with deionized water and acetone, and finally dried in an oven for 24 h to reach a constant mass. The Polyaniline-Copper oxide composites were thus obtained containing 50wt %(*i.e.50*%weight percentage of Copper oxide) [13].

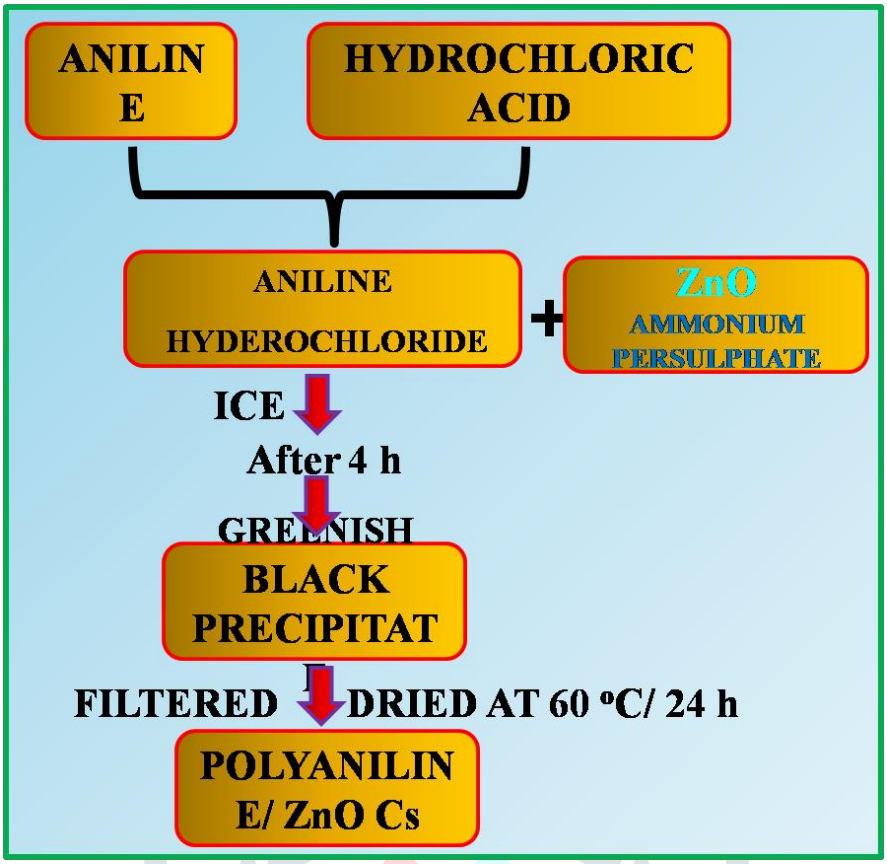

Fig.2. Flowchart for the synthesis of Polyaniline/ZnO composites.

3. XRD ANALYSIS

X-Ray Diffraction were studies using Shimadzu-7000 diffractometer with Cu as the target (1.54 Å) and nickel as the filter. Fig.3 Observed diffraction pattern of Polyaniline. A broad peak centered at $2\theta = 25.53^0$ may be assigned to the scattering from the Polyaniline chains at interplanar spacing which clearly implies the amorphous nature of Polyaniline and it corresponds to diffraction planes (200) of pure Polyaniline [13-14].

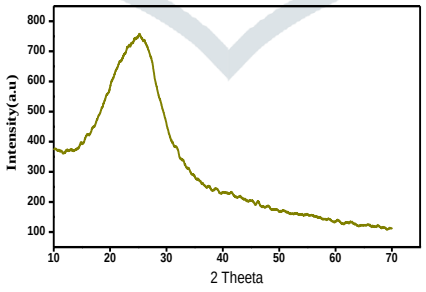

Fig.3. XRD Pattern of pure Polyaniline.

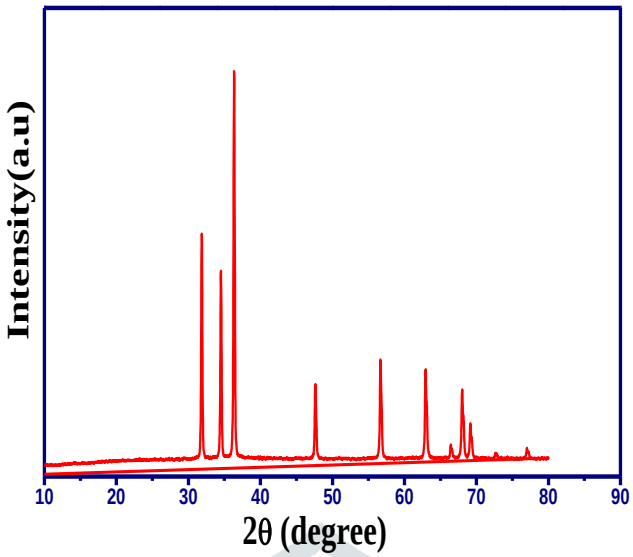

Fig.4. XRD Pattern of Zinc oxide particles.

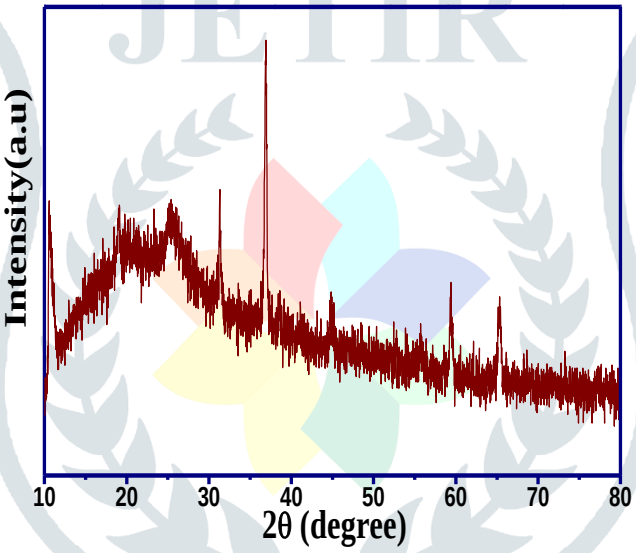

Fig.5. XRD Pattern of Polyaniline copper oxide composites.

Fig.4 Shows a broad peak at $2\theta=16^0$,37^0& 49.75^0 57.35^0, 63.75^0, 68.5^0which has a sharp and well defined peak and it indicates good crystallinity of ZnO particles Fig.5 shows the intensity of diffraction peaks for PANI/ZnO composites and it is found to be lower than that for pure Zinc oxide particles. The peaks of pure copper oxide particles are also present in PANI/ZnO composites. The amorphous background hump comes from the Polyaniline [15].

4. SEM MICROGRAPH

The morphology of the materials were recorded using a scanning electron microscope (Hitachi table top, Model TM 3000) operated at an accelerating voltage of 15 kV. **Fig.6(a)** shows SEM micrographs of pure Polyaniline. It can be seen from the figure that the pure Polyaniline is poorly adsorbed on the surface with no ZnO particles. **Fig.6(b)** depicts the SEM micrographs of ZnOparticles, It can be seen from the figure that the ZnOparticles were agglomerated, irregular in nature and this agglomeration was due to trapping of Cu-O bonding. As we concentration of ZnO increase the SEM micrographs show more and more number of particles deposited on the surface of Polyaniline layer [16-18] **(Fig.6(c)).**

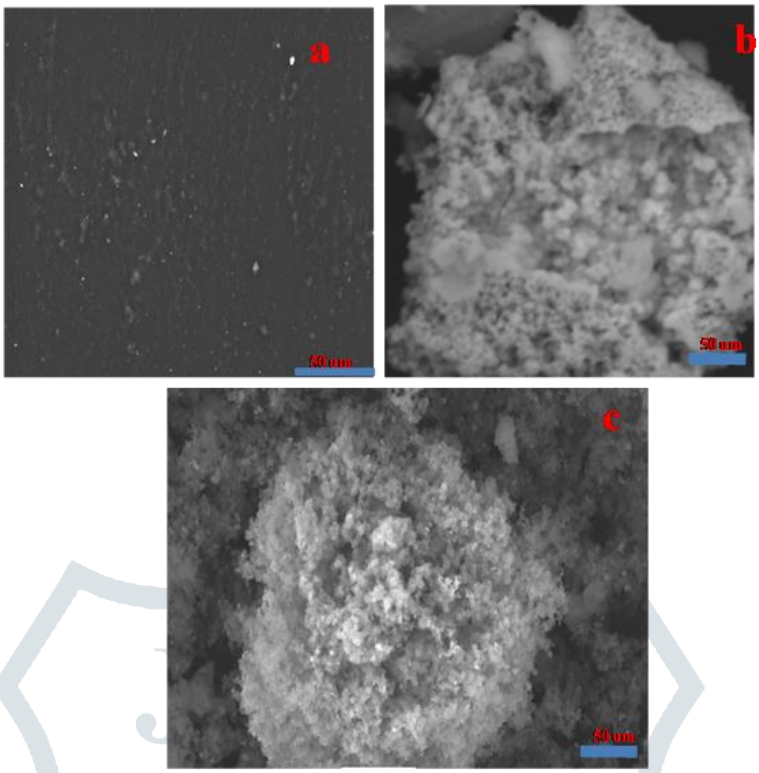

Fig.6. SEM Micrographs of (a) Polyaniline, (b) Pure ZnO Particles & (c) PANI/ZnO(50 wt %) composites

5. DC Conductivity of Pani/ZnO composites

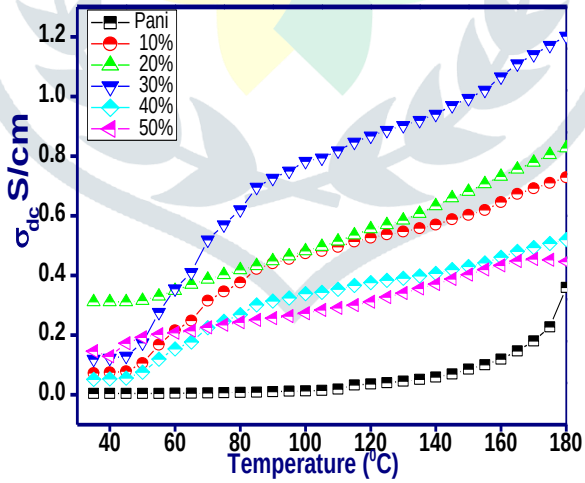

Fig.7. DC Conductivity of Polyaniline zinc oxide composites.

The dc conductivity of the Polyaniline/ZnO composites was studied by using Keithley 6514 electrometer. The plot of dc conductivity of PANI and PANI/ZnO composites with temperature dependent are shown in Fig.7. The conductively is found to increase as a function of increase in temperature. This increase in conductivity with temperature is the characteristic of "thermal activated behavior". The increase in

conductivity could be due to increase of efficiency of charge transfer between the polymer chains and the dopant with enhancement in temperature. The thermal curing effects of the alignment of polymer chain, which leads to the increase of conjugation length possibly also brings about increase in the conductivity of the composites [17-22].

5. AC Conductivity of Pani/ZnO composites

Fig.8 shows the variation of ac conductivity as a function of frequency for Polyaniline/ZnO composites for (10 to 50wt %) performed in RT. It is observed that σ_{ac} remains constant up to 104 Hz. Polyaniline /ZnO40 wt % composites shows high conductivity due to interfacial polarization and concentration of charge carriers enhanced. However, in case of pure Polyaniline and other composites with Polyaniline conductivity is comparatively high. The conductivity of PANI/ZnOcomposites increases due to the distribution of ZnO particles in Pure Polyaniline [15-22].

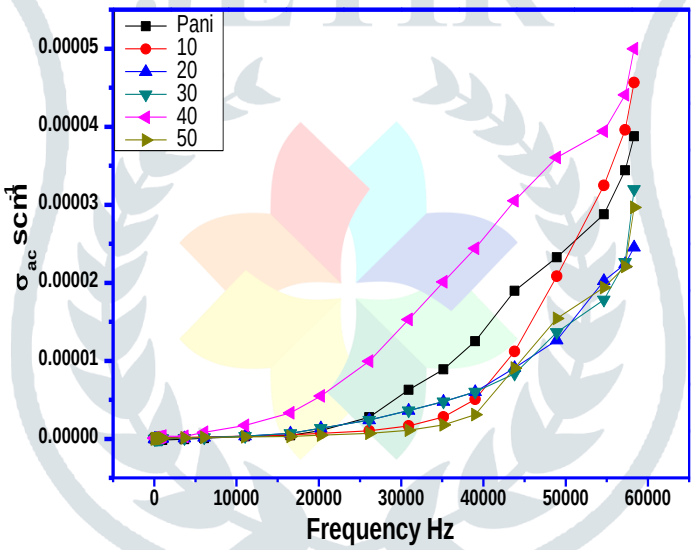

Fig.8. AC Conductivity of Polyaniline zinc oxide composites.

6. Sensor studies of PANI / ZnO composites.

A gas sensor is a chemical sensor that is operated in the gas phase. It converts chemical information, which is determined by different concentrations of gaseous chemical species, into an electrical signal. In case of polymer / metal oxide composites both the polymer sensing mechanism of swelling and metal oxide sensing mechanism of surface charge as presented earlier [21] are responsible for variation of resistance with in the sensing material. On careful observation of Figure 9, it is found that change in sesitivity of 40 & 50 wt % of ZnO in PANI is very high compared with PANI and this may be due to presence of capillary pores as reviled revealed by SEM. All the composites have shown same behaviour as pure PANI. The Fig.9 shows 40 & 50 wt % of ZnO in PANI composite has high sensitivity for LPG, hence it is found to be promising LPG sensing material for the design of sensing device [21].

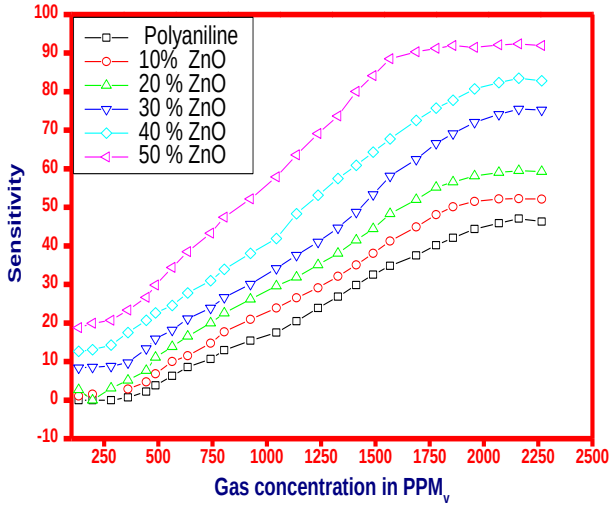

Fig.9. Change in Sensitivity versus Gas concentration (PPMV) of PANI / ZnO composites.

6. CONCLUSIONS

Pure and Pani/ZnO composites were successfully prepared by in-situ polymerization technique. The composites showed high crystalline nature with no impurity peaks. The surface morphology of the composites were studied by means of SEM and the results showed agglomeration of particles. variation of ac conductivity as a function of frequency for Polyaniline/ZnO composites for (10 to 50wt %) performed in RT. The increase in AC and DC conductivity could be due to increase of efficiency of charge transfer between the polymer chains and the dopant with enhancement in temperature. Polyaniline /ZnO40 wt % composites shows high conductivity due to interfacial polarization and concentration of charge carriers enhanced. 40 & 50 wt % of ZnO in PANI composite has high sensitivity for LPG, hence it is found to be promising LPG sensing material for the design of sensing device. All these results together reveal that the synthesized composites can be used in the field of electrical applications.

References

[1]. Hajeebaba K Inamdar, H. Nagabhushana, Basavaraja Sannakki, R.D. Mathad , DC Conductivity Study of Polypyrrole/Cr2O3 Nanocomposites prepared through Green Synthesis Materials Today: Proceedings 3 (2016), pp3850–3854.

[2]. R. L. N. Chandrakanthi,M. A. Careem, Preparation and characterization of CdS and Cu2S nanoparticle/Polypyrrole composite films, Thin Solid Films, 417(2002), pp- 51-56.

[3]. Sharanabasamma M Ambalagi, Hajeebaba K Inamdar and Basavaraja Sannakki,Materials Mechanism of DC Conductivity Measurement of Zinc Oxide Doped Polypyrrole Nanocomposites Today: Proceedings 3 (2016), pp3945–3950.

[4]. Ali Fakhri , Sajjad Behrouz, Mohammad Asif , Inderjeet Tyagi , Shilpi Agarwal, Vinod Kumar Gupta, “Synthesis, structural and morphological characteristics of Cr2O3

nanoparticles Co-doped with boron and nitrogen" , Journal of Molecular Liquids 213 (2016) 326–331.

[5]. Y. He, Synthesis of Polypyrrole/nano-CeO2composite microspheres via a solid – stabilized emulsion route, Mater. Chem. Phys, 92, (2005), pp134- 137.

[6]A. G. MacDiarmid, L. S. Yang, W. S. Huang, B. D. Humphrey, Polyaniline: electrochemistry and application to rechargeable batteries, Synth. Met.,18,(1987), PP- 393- 398.

[7] D Navami, RB Basavaraj, GP Darshan, Hajeebaba K Inamdar, SC Sharma, HB Premkumar, H Nagabhushana, Evolution of shapes and identification of level II and III features of fingerprints using CaZrO3: Sm3+ fluorescent markers prepared via solution combustion route, Optical Materials, 88 (2019), 479-487

[8]D. Verma, V. Datta, Role of novel microstructure of polyaniline-CSA thin film in ammonia sensing at room temperature, Sens. Actuat. B,134,(2008) PP-373-376.

[9]. S Farheen, F Jahan, HK Inamdar, RD Mathad, "Effect of polymer blending on mechanical and thermal properties", Modern Applied Science, (2015),12 (1), pp 520-22

[10]. SM Ambalgi, HK Inamdar, VT Manjula, SG Sannakki Nagaraja," Synthesis, Characterization and Electrical Properties of Polypyrrole/ChromiumOxide Nanocomposites", International Journal of Engineering Research (2016), 5 (2), pp 119-122

[11]. M. P. Pileni, "Magnetic fluids: fabrication, magnetic properties, and organization of nanocrystals," Advanced Funtional Materials", Vol.11, (2001), pp-323–336.

[12]. Pallavi T. Patil*, Rajshri S. Anwane, Subhash B. Kondawar, Development of electrospun polyaniline/ZnO composite nanofibers for LPG sensing, Procedia Materials Science 10 (2015) 195 – 204

[13]. Hajeebaba K Inamdar, Arjun N Shetty, S Kaveri, Basavaraj Sannakki, MVN Ambikaprasad, *Aloe vera* (L.) Burm. F Assisted Green Synthesis and Biological Applications of Y_2O_3:Mg^{2+}Nanocomposites, Journal of Cluster Science (Springer US) 29, 4, 2018, 805-813

[14] Rajesh Siddanna, Hajeebaba K Inamdar, Archana Mugalgaon, MVN Ambikaprasad, "Green Synthesis of MgO Nanoparticles their Structural and Biological Applications", International Journal of Scientific Research in Science, Engineering and Technology 4 (1), (2018),831-834.

[15] V. Ponnarasan and A. Krishnan, " Studies on Pure and Divalent Metal Doped Copper Oxide Nanoparticles", Adv. Studies Theory Phys.,vol.8, no. 6, 251-258, 2014.

[16] Wei Chen, Gary C. Lickfield and Charles Q. (2004). Yang polymer 45(3), 2004, P 1063-1071.

[17] Hajeebaba K Inamdar, M.Sasikala, Dayanand Agsar, M.V.N. Ambika Prasad, Facile green fabrication of ZnO nanopowders: Their antibacterial, antifungal and photoluminescent properties, Materials Today: Proceedings 5 (2018) 21263–21270

[18] S. A. Chen, K. R. Chuang, C. I. Chao, H. T.Lee, White light emission from electroluminescence diode with polyaniline as the emitting layer, Synth. Met.,82,(1996)PP-207-210.

[19] L.Y. Yuan, B. Yao, B. Hu, K.F. Huo, W. Chen, J. Zhou, Polypyrrole-coated paper for flexible solid-state energy storage, Energy Environ. Sci. 6 (2013) 470–476.

[20]S. Hossein Hosseini1, S. Hossein Abdi Oskooei, and Ali Akbar Entezami, Iranian Polymer Journal, 14 (4), (2005) 333-344.

[21] Devidas Ramrao Patil and Lalchand Avachit Patil, IEEE Sensors Journal, Vol. 7, No. 3, March 2007.

[22] Hajeebaba K Inamdar, MVN Ambika Prasad, RB Basavaraj, M Sasikala, SC Sharma, H Nagabhushana, Promising red emission from functionalized Polypyrrole/CaTiO3: Eu3+ nano-composites for photonic applications, Optical Materials, 88 (2019), 458-465