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Polyindole Based Zinc Oxide Nanocomposite-Synthesis and Characterization

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Abstract:- **In the present work polyindole based zinc oxide nanocomposite was prepared. Here zinc oxide nanoparticles were prepared separately using well-known wet-chemical method. Polyindole based zinc oxide nanocomposite was prepared using chemical oxidative polymerisation method. Polyindole was also prepared separately from its monomer indole to compare their properties with their counter parts. The samples have been analysed using UV, FTIR, XRD and CV techniques.The surface morphology is investigated with SEM and AFM analysis. FTIR studies showed that there is strong interaction between polyindole and nano sized Zinc Oxide particles. The AFM image showed by Polyindole picture was changed entirely in the case of nanocomposite. FTIR showed the vibration bands of both polyindole and zinc oxide in the nanocomposite. From the XRD spectrum the particle size was calculated using Scherrer's equation.**

Key Words: chemicaloxidativepolymerisation, morphology, nanocomposite, polyindole, XRD.

I. INTRODUCTION

Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nanometers. Nanoscience and nanotechnology are the study and application of extremely small things and can be used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering. Physicist Richard Feynman said "There's Plenty of Room at the Bottom" the ideas and concepts behind nanoscience and nanotechnology were started by this. Today's scientists and engineers are finding a wide variety of ways to deliberately make materials at the nanoscale to take advantage of their enhanced properties such as higher strength, lighter weight, increased control of light spectrum, and greater chemical reactivity than their larger-scale counterparts. S. Tom Picraux said Nanotechnology is highly interdisciplinary, involving physics, chemistry, biology, materials science, and the full range of the engineering disciplines. Nanocomposites are solid materials that have multiple phase domains and at least one of these domains has a nanoscale structure. The materials can have novel chemical and physical properties that depend on the morphology and interfacial characteristics of the component materials. Nanocomposites have gained much interest recently. Significant efforts are underway to control the nano structures via innovative synthetic approaches. The properties of nanocomposite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics [1], [2]. In the large field of nanotechnology, polymer matrix based nanocomposites have become a prominent area of current research and development [3]. Polymer nanoscience is the study and application of nanoscience to polymer-nanoparticle matrices, where nanoparticles are those with at least one dimension of less than 100 nm [4]. Conjugated polymers like polyaniline, polypyrrole, polythiophene (Ferraro, 1987) and their substituted derivatives have received a great deal of attention because of their good electrical properties, environmental stability and ease of synthesis [5], [6]. A number of other heterocyclic polymers namely polyindole, polycarbazole, polyfuran, polyisothionaphthene and polyphenazine are also continue to be developed and studied [7]-[12]. The basic conduction mechanism in conducting polymers is due to Polarons, Bipolarons and solitons [13]. The first report on the electrochemical formation of polyindole was made by Tourillon et al [14]. Polyindole has air stability and its conductivity is about 10-3–10-1 S cm-1 depending upon the synthetic technique and the nature of dopant ions. This is usually obtained by the anodic oxidation of indole under suitable conditions [15]. Different transition metal oxides such as copper, iron, nickel, cobalt and zinc ranging from micrometer to nanometer size materials are of current research interest due to several possible applications in photonics, sensors, catalysis, drug delivery systems, optical switching devices etc. [16]. Recently, conducting polymer/metal oxide nanocomposites have been considered as a new class of materials due to their improved properties when compared with those of pure conducting polymer and metal oxide [17]. Zinc oxide has received tremendous attention due to its interesting properties like direct band gap of 3.41 eV. Due to its unique optical and electrical properties, it is regarded as a promising material in optoelectronic applications [18]-[20]. The aim of this study was to develop conducting polymer nanocomposites for

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Vol 3, Issue 4, April 2018

electrocatalytic application and this was done by polymerization of indole incorporated with ZnO nanoparticles.

II. EXPERIMENTAL

Materials

Indole, acetonitrile, Ammoniumperoxodisulphate, Sodium hydroxide, Zinc sulphate heptahydrate and deionized water were used to synthesis nanoparticles, polymer and polymer nanocomposite.

A. Synthesis of Polyindole

Indole (0.1M, monomer) was dissolved in acetonitrile (1ml) and Ammoniumperoxodisulphate (APS as oxidant, 0.1M) was added drop wise to the above solution under stirring. The colour of the reaction mixture was changed from colourless to dark green due to polymerization. After 10 hours the reaction mixture was filtered and washed with water to remove unreacted indole monomer, ammoniumperoxodisulphate and acetonitrile. Polyindole was collected and dried in room temperature.

B. Synthesis of ZnO nanoparticle

Sodium hydroxide (NaOH, 1M) was added slowly into the zinc sulphate heptahydrate (ZnSO4.7H2O, 0.1M) solution under stirring then refluxed for 2 hr, the white precipitate of zinc hydroxide was filtered and washed with water to remove impurities. Dried ZnO nanoparticles were collected at room temperature.

C. Synthesis of ZnO doped Polyindole nanocomposite

Indole (0.1M, monomer) was dissolved in acetonitrile (1ml) and Ammoniumperoxodisulphate (APS as oxidant, 0.1M) was added drop wise to the above solution under stirring. The ZnO (1g) nanoparticles were added to the monomer solution and and stirring was continued. After 10 hr the polyindole-ZnO nanocomposite was thoroughly washed with water to remove unreacted indole monomer, ammoniumperoxodisulphate and acetonitrile. Polyindole-ZnO nanocomposite was dried at room temperature.

III. RESULT AND DISCUSSIONS

A. UV Spectrum Analysis

The optical characterization of the sample was recorded on UV-Vis absorption spectrophotometer. Fig.1 shows the UV-Visible absorption spectra of ZnO nanoparticles as a function of wavelength. The peak finds at 363 nm. Band gap of ZnO nanoparticle 3.41eV [21] The absorption band of the ZnO nanoparticles shows a blue shift due to the quantum confinement of the excitations present in the sample as compared with the bulk ZnO particles. This optical phenomenon indicates that these nanoparticles have a quantum size effect [22].

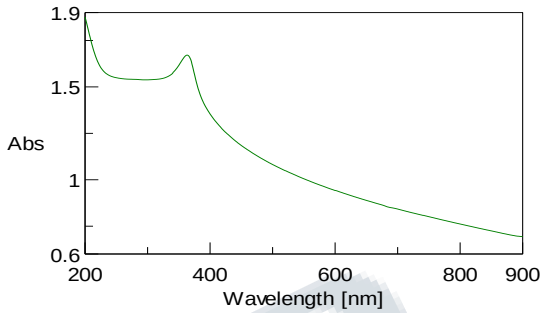

Fig.1 UV Spectra of ZnO Nanoparticle

Fig.2 shows the UV-Visible absorption spectra of polyindole. The 214 nm peak corresponds to π-π* transitions of the polymer chain [23] and, the peaks at 273nm, 349nm and 448 nm belong to conjugation and π-π* transitions of benzene ring [24].

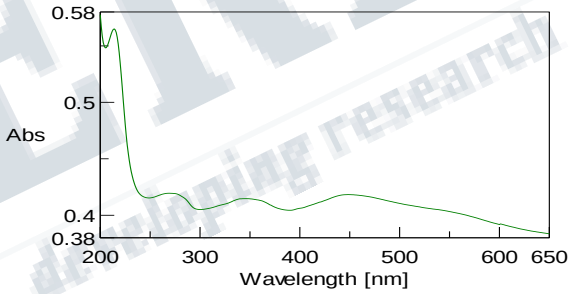

Fig.2 UV Spectra of Polyindole

Fig.3 shows UV-Visible absorption spectra of Polyindole-ZnO nanocomposite. Peaks at 241 nm, 317 nm, 367 nm, 418 nm indicates ZnO inserted in polyindole matrix. Peaks at 241 nm, 317 nm, 367 nm due to to π-π* transitions and 418 nm refers to n-π* transitions, it signifies the formation of polarons which depends on amount of metal oxide [25].

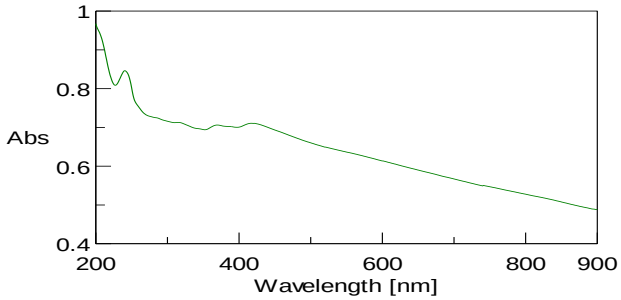

Fig.3 UV Spectra of Polyindole-ZnO nanocomposite

ISSN (Online) 2456 -1304

International Journal of Science, Engineering and Management (IJSEM)
Vol 3, Issue 4, April 2018

B.FTIR Spectrum Analysis

In FTIR, the intensity-time output of the interferometer is subjected to a Fourier Transform to convert it to the families infra-red spectrum i.e., intensity frequency. The identification of the atomic arrangement and the concentrations of the chemical bonds present in the samples have been carried using Fourier Transform Infra-red Spectroscopy (FTIR), Model P-4600 (Thermoscientific make) instrument in which percentage transmission and wave number are the output.

Fig.4 shows FTIR spectrum of Polyindole. Spectrum of Polyindole [26-28] and ZnO nanoparticles [29] are similar to that already reported. A sharp band at 739.27 cm−1 is due to the characteristic out-of-plane-deformation of the CH bond in the benzene ring of indole [30], [31]. Peak at 1107.74 cm−1 indicates Vibration mode of C – N bond [32]. The band located at 1177.76 cm−1 has been assigned to the in-plane CH bonding modes present in aromatic heterocyclic part of indole [33]. Peak at 1331.21 cm−1 indicates Stretching modes of pyrrole ring [34], [35]. The sharp spectral band at 1451 cm−1 and 1381.21 cm−1 are attributed to the vibration mode of the C–N and C=N stretching respectively [36]. The presence of C-N vibration modes supports the fact that the nitrogen atom of indole is not involved in the polymerization process. Peak at 1566.30 cm−1 and 1612.16 cm−1 indicates C-C stretching vibration [37] of benzenoid ring of indole. The intense IR band located at 3390 cm−1 is the N–H stretching vibration. The vibration band of hydrogen species due to the C2 and C3 of the indole unit [37] ought to be present at 720 cm−1 is absent, suggesting that 2, 3 position of the pyrrole ring of indole is the favored polymerization site for indole.

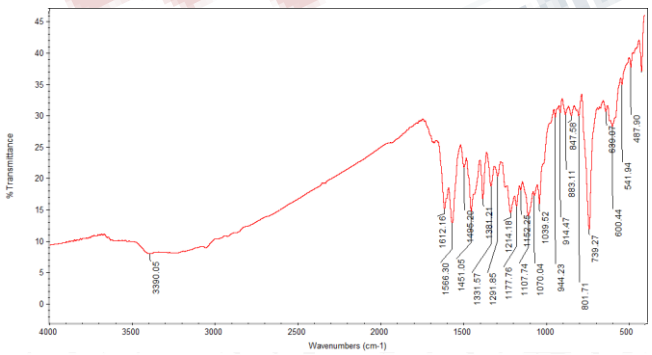

Fig.4 FTIR Spectrum of Polyindole

Fig.5 shows FTIR spectra of ZnO nanoparticles. Infrared studies were carried out in order to ascertain the purity and nature of the metal nanoparticles. Metal oxides generally give absorption bands in fingerprint region i.e. below 1000 cm-1 arising from inter-atomic vibrations. The peak observed at 3441.44 cm−1 and 1173.86 cm-1 are may be due to O-H stretching and deformation, respectively assigned to the water adsorption on the metal surface. The peaks at 1631.55 cm−1, 880.56 cm-1 are corresponds to Zn-O stretching and deformation vibration, respectively. The metal-oxygen frequencies observed for the respective metal oxides are in accordance with literature values [38] – [40].

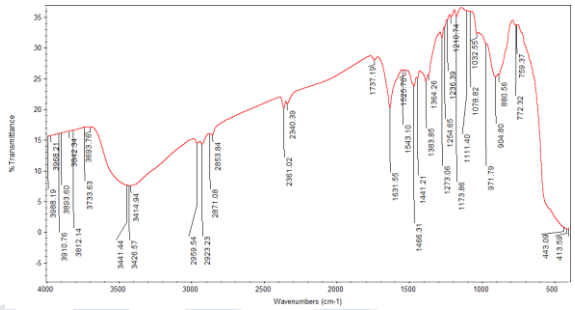

Fig.5 FTIR Spectrum of ZnO nanoparticles

Fig.6 shows Polyindole-ZnO nanocomposite. The shift in some peaks, in the frequency range of 1100 cm−1–1600 cm-1 (due to different stretching vibrations of benzene rings) [41], [42] such as 1114.07 cm−1 (vibration mode of C–N bond) and 1486.34 cm−1 (stretching mode of benzene ring) and the peak at 502.60 cm-1 corresponds to the characteristic signal of Zn-O of ZnO nanoparticles which indicates a significant interaction of ZnO nanoparticles with the polymer.

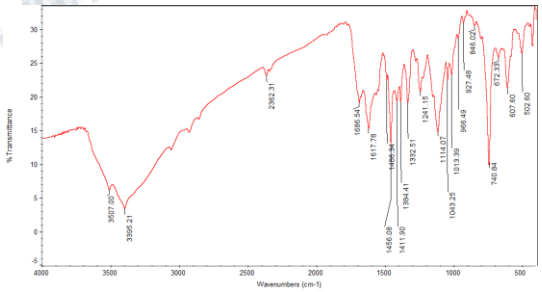

Fig.6 FTIR Spectrum of Polyindole-ZnO nanocomposite

C. X-ray Diffraction Analysis

Fig.7, Fig.8 and Fig.9 demonstrates the XRD patterns of the synthesized ZnO nanoparticles, Polyindole and ZnO doped Polyindole nanocomposite. The X-ray diffraction data were recorded by using Cu Kα radiation (1.5406 Angstrom). The intensity data were collected over a 2θ range of 20–80°. The average grain size of the samples was estimated with the help of the Scherrer equation, using the diffraction intensity of (101) peak. X-ray diffraction studies confirmed that the synthesized materials were ZnO with wurtzite phase and all the diffraction peaks agreed with the reported JCPDS data;

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Vol 3, Issue 4, April 2018

no characteristic peaks were observed other than ZnO. The mean grain size (D) of the particles was determined from the XRD line broadening measurement using the Scherrer Equation.

$D = 0.89\lambda/(\beta Cos\theta)$

Where λ is the wavelength (Cu Kα), β is the full width at the half- maximum (FWHM) of the ZnO (101) line and θ is the diffraction angle. A definite line broadening of the diffraction peaks is an indication that the synthesized materials are in the nanometer range. The lattice parameters calculated were also in agreement with the reported values. The reaction temperature greatly influences the particle morphology of as-prepared ZnO powders [43].

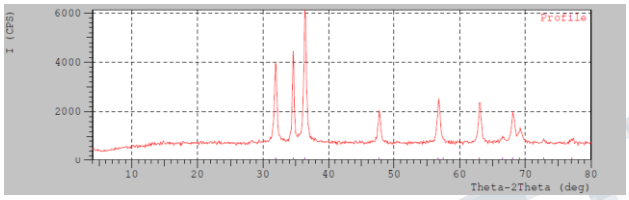

Fig.7 XRD patterns of ZnO nanoparticles

The XRD pattern of PIn exhibited broad diffraction peaks, suggesting that the PIn was amorphous. Earlier also, PIn has been proposed as amorphous polymer [44].

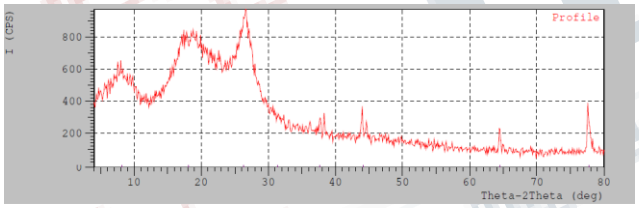

Fig.8 XRD patterns of Polyindole

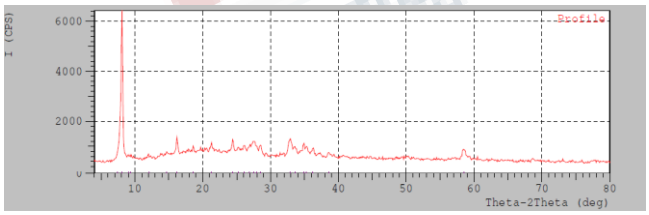

Fig.8 XRD patterns of ZnO doped Polyindole Nano composite

The results of size measurement showed that the crystallite size of ZnO Nanoparticles, Polyindole, ZnO doped Polyindole were found to be 38 nm, 3.7 nm and 25 nm respectively.

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D. Cyclic Voltammetry

Cyclic voltammetry is one of the most versatile electroanalytical techniques for the study of redox behavior of electroactive species. Electrochemical measurements of Cyclic voltammetric studies were conducted using a CHI 650C electrochemical workstation with conventional three electrode cell at room temperature. A three electrode cell assembly with Pt-wire electrode as counter electrode, Modified Zinc oxide or polindole or ZnO doped polyindole nanocomposite-glassy carbon electrode or GCE for comparison, was employed as the working electrode. A silver/silver chloride (Ag/AgCl) electrode acted as the reference electrode. The supporting electrolyte was 0.1 M KCl [45], [46]. To investigate the electrochemical performance of zinc oxide modified glassy carbon electrode, cyclic voltammetry (CV) was employed over a potential range from +1 to -1 volt. Cyclic voltammetric behavior of ZnO nanoparticle showed one oxidation peak at 0.2704 V and one reduction peak at 0.0597 V as shown in Fig.9

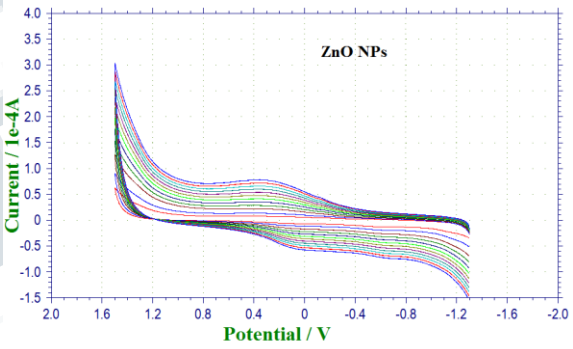

Fig.9 Cyclic voltammetric studies of ZnO nanoparticle at differtent scan rates

Cyclic voltammetric behavior of Polyindole showed one oxidation peak at 0.4083 V and two reduction peaks at 0.1574 V and -0.5909 V and it was shown in Fig.10

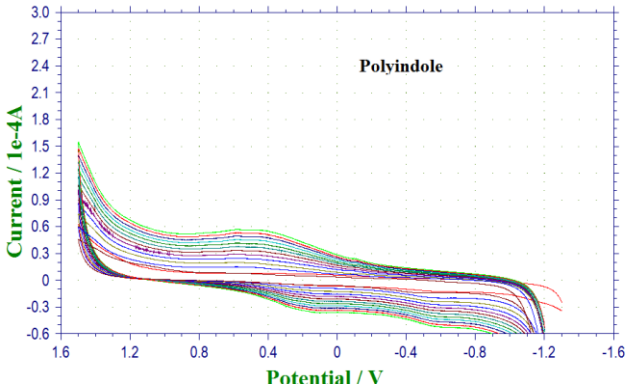

Fig.10 Cyclic voltammetric studies of Polyindole at differtent scan rates

ISSN (Online) 2456 -1304

International Journal of Science, Engineering and Management (IJSEM)
Vol 3, Issue 4, April 2018

Cyclic voltammetric behavior of ZnO doped Polyindole showed three oxidation peaks at 0.5295 V, 0.3729 V and -0.1365 V and two reduction peaks at 0.0789 V and -0.6263V and it was shown in Fig.11.

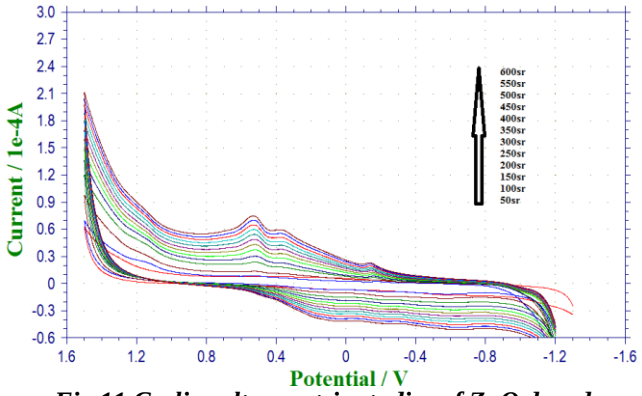

Fig.11 Cyclic voltammetric studies of ZnO doped Polyindole at differtent scan rates

E. Pseudo Capacitve Behaviour -Bode plot

The Bode plot is shown in Fig.12 and it represents the change in the Bode phase with applied frequency. The phase angle θ can vary between 90o (for a perfect capacitor n = 1) to 0o (for a perfect resistor n = 0) [47]. The value of n is obtained from the slope of frequency versus |Z| plot. In the case of ZnO nanoparticles the phase angle of 800 indicates the pseudo capacitive nature of the material. The plot of log |Z| versus log f (Hz) (Fig.15) also gave a slope value in the range of 0.4-0.6 (R^2 = 1.000) suggesting the pseudo capacitive behaviour of Zinc oxide [48].

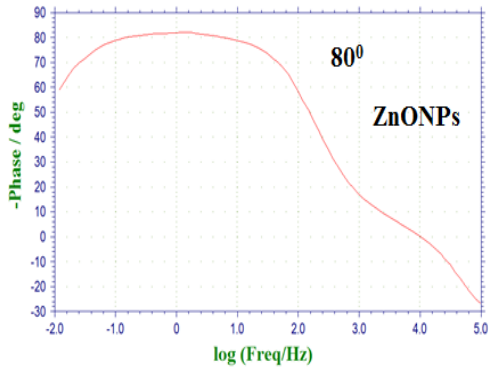

Fig.12 Bode plot of -phase angle/ deg. versus log (f/Hz)) for ZnO nanoparticles

As per Bode plot (-phase angle (degree) vs. log f(Hz) shown in Fig.13, the bode phase angle for Polyindole is closed to 78o which is lower than that for nano Zinc oxide(80o), Polyindole exhibits better pseudocapacive behaviour thanPolyindole. As seen from Bode plot as shown in Fig.16, at the slope value for Polyindole is 0.6(R2=1) at the low frequency region. It indicates the characteristic of a pseudo capacitor.

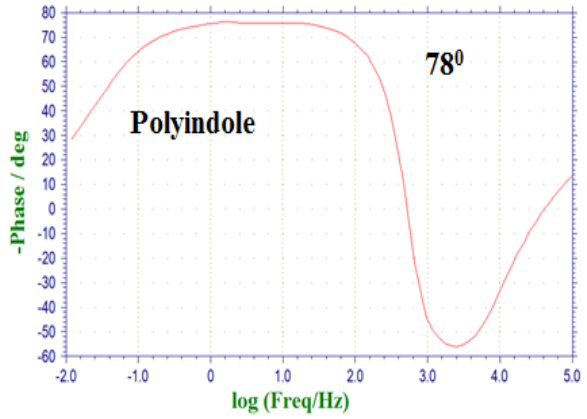

Fig.13 Bode plot of -phase angle/ deg. versus log (f/Hz)) for Polyindole

As per Bode plot (-phase angle (degree) vs. log f(Hz) shown in Fig.14, the bode phase angle for ZnO-Polyindole nanocomposite is closed to 84o which is larger than that for nano Zinc oxide(80o) and Polyindole(780) exhibits better pseudocapacive behaviour than Polyindole and nano ZnO. As seen from Bode plot as shown in Fig.17, at the slope values for ZnO-Polyindole nanocomposite is 0.7(R^2=1) at the low frequency region. It indicates the characteristic of a pseudo capacitor.

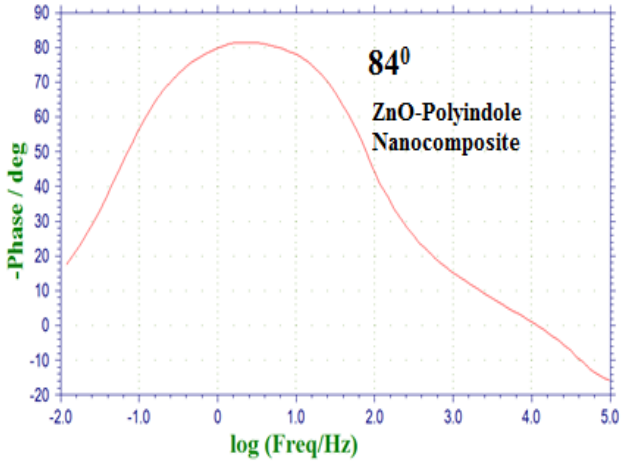

Fig.14 Bode plot of -phase angle/ deg. versus log (f/Hz)) for ZnO doped Polyindole

ISSN (Online) 2456 -1304

International Journal of Science, Engineering and Management (IJSEM)
Vol 3, Issue 4, April 2018

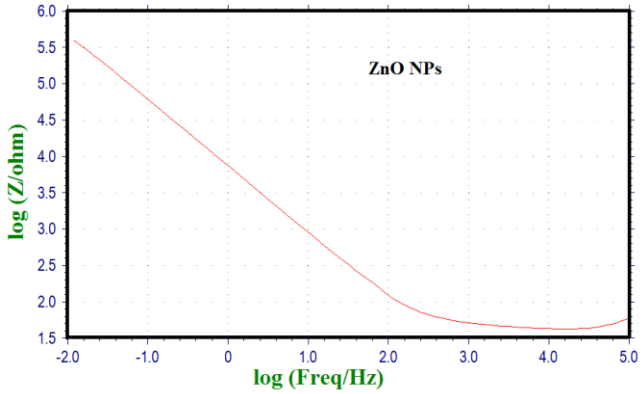

Fig.15 Bode plot of log |Z/ohm| versus log (f/ Hz) forZnO nanoparticles

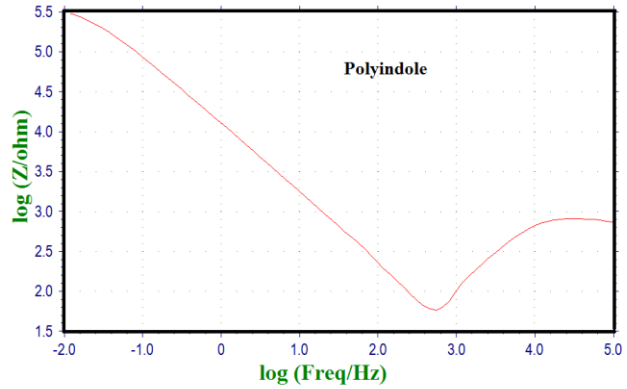

Fig.16 Bode plot of log |Z/ohm| versus log (f/ Hz) for Polyindole

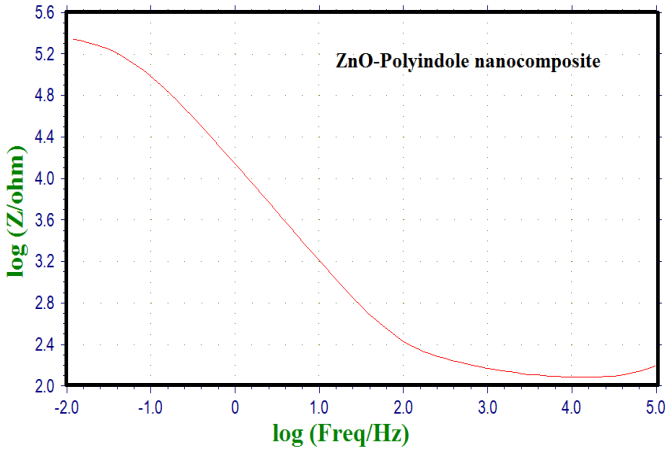

Fig.17 Bode plot of log |Z/ohm| versus log (f/ Hz) for ZnO-Polyindole nanocomposite

CONCLUSION

ZnO nanoparticle, Polyindole and polyindole-ZnO nanocomposite were prepared successfully by chemical oxidative polymerization method. The characterizations of prepared samples were done by UV Spectroscopy, FTIR, XRD analysis. FTIR revealed that the peak at 502.60 cm-1, 1114.07 cm -1 (vibration mode of C–N bond) and 1486.34 cm -1 (stretching mode of benzene ring) were assigned to the characteristic signal of a significant interaction of ZnO nanoparticles with the polymer polyindole.From XRD analysis the crystallite size of ZnO Nanoparticles, Polyindole, ZnO doped Polyindole were found to be 38 nm, 3.7 nm and 25 nm respectively.

Electrochemical studies have also been carried out. The glassy carbon electrode coated ZnO-Polyindole nanocomposite exhibited excellent capacitive performance and a high specific capacitance between −0.2 and 2.0V in 0.1M H2SO4 electrolyte. This capacitive performance is due to synergistic effect of large surface area and high pseudo-capacitive reaction by the presence of ZnO-Polyindole nanocomposite. Thus ZnO-Polyindole nanocomposite was considered as suitable electrode materials for supercapacitors. The capacitance of chemically synthesized nanocomposite suggests that, they can be used for electronic applications.

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