Fabrication, Characterization and Gas Sensing Behavior of $BaCuO_2$ Doped Polypyrrole Nano Composite Thin Films

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Abstract - A series of Ppy-$BaCuO_2$ polymer nanocomposite films were synthesized by the dissolving Ba-doped CuO by weight % (5, 10, 15, 20 and 25%) in polypyrrole(Ppy) solution (1:1) using chemical polymerization technique. All the nanocomposite films (XRD) X-ray diffraction, (IR) infrared spectroscopy and (SEM) scanning electron microscopy were used to identify the datas, electrical conductivity measurements. It is clear from the intensity of the diffraction peaks increases with increasing $BaCuO_2$ doped polypyrrole sample XRD patterns the a rise in the concentration of $BaCuO_2$. These conclusion are also in good accordance with the morphological changes observed in the $BaCuO_2$ doped polypyrrole samples, as per the SEM analysis, The rise in conductivity increasing the concentration of $BaCuO_2$ has been observed in Ppy-$BaCuO_2$ composites. The NH_3 gas was used to study the gas sensing behavior of investigated films.

Keywords: Thin films, Sensors, X-ray, Current, voltage, composites

I. INTRODUCTION

Polymer blending is the best effective method for creating materials with a wide range of qualities and it is one of the most modern approaches to the development and design of novel polymeric nanocomposite blend materials [1]. The thermal resistance of composite hosts is considerably increased when inorganic Nano-fillers are added to the mix [2]. Fibers with a higher hemicellulose percentage absorb more moisture, resulting in the production of char is often fibres are better with a higher lignin concentration because they degrade at lower temperatures [3]. Because of its hierarchical structure and semi-crystalline form, cellulose is isolated from natural fibres and employed in the manufacturing of composites for reinforcing. Polymeric/inorganic nanocomposites are frequently significantly destroyed at greater temperatures than virgin composites [4], showing a significant drop in the degradation rate [5]. As a result, even if just a modest number of nano-fillers is loaded, the thermal resistance of composite hosts can be significantly improved [6]. Polypyrrole [Ppy] is among the most studied inherently conducting polymers among conjugated polymers. As a result of ease of manufacture, superior environmental stability, veriable electrical conductivity, and facile doping / dedoping behaviour, PPy has a high scientific value. Conductivity in metal-polymer complex is affected by a no. of parameters, including the oxidant-to-monomer proportion, particle loading concentration, filler shape, size, compactness, and interfacial interactions between the filler molecule and the host composite [7]. SnO_2, ZnO, CeO_2, V_2O_5, TiO_2, fly ash, Fe_3O_4, ZrO_2 composites [8-11] ZnO, one of these transition metal oxides, has sparked a lot of concern with the manufacture of PPy hybrid composites due to its wide range of optoelectronic device advantages. CuO nanoparticles doped with Ba may be incorporated into PPy to create a novel material with valuable characteristics. FTIR, XRD, SEM, and UV-Vis spectra were used to explore the effect of dopants on the microstructure and electrical characteristics of composites in this study.

II. EXPERIMENTAL

A. Preparation of Ba-doped CuO nanoparticles by electrochemical procedure:

The simple, cost-effective electrochemical approach is used to make nanoscale Ba-doped CuO nanoparticles using $BaCl_2$, in an aqueous system, a copper electrode is used with $NaHCO_3$ as the conducting salt, a platinum electrode is used. An electrochemical process according to the electrolytic cell where The copper electrode acted as an anode, while the platinum electrode acted as a cathode, with a distance between two points is 1cm. The electrolytic solution was optimised to incorporate 20 ml of 0.5% $NaHCO_3$ in the electrolytic solution 0.05g $BaCl_2$. Using a

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DC source and a current of 12mA, a potential difference was applied between the electrodes, and the synthesis was carried out in a galvanostatic manner at room temperature without stirring for 3hours. The electrochemical synthesis of the creation of Ba-doped CuO nanoparticles is caused by the dissolution of copper electrodes, which releases Cu^{2+} ions, which are electrochemically reacted with $NaHCO_3$ solution to create CuO, followed by barium occupying the interstitial lattice of CuO, resulting in Ba-doped CuO nanoparticles. Because the synthesis is optimised to 20 ml of $NaHCO_3$ solution, the yield of nanoparticles obtained is 0.5-1g. To obtain the appropriate amount of nanoparticles, the reaction can be repeated under the same experimental circumstances. The received nanoparticles are centrifuged and calcined after being rinsed with distilled water until all sodium bicarbonate is removed at 500 oC for 2 hours for complete elimination of sodium and hydroxide impurities, then utilized for the preparation Ppy-Ba/CuO polymer nanocomposite films.

B. Preparation of Ppy-$BaCuO_2$ polymer nanocomposite films:

The 0.05 g of Ba-doped CuO was dispersed in a 0.5 M aqueous $FeCl_3.6H_2O$ solution in distilled water for half an hour. Then, to polymerize the pyrrole monomer, 0.2 mole solution of pyrrole was added dropwise to the corresponding mentioned mixture and agitated for 3hrs to obtain the composite. Other PPy samples with varied Ba-doped CuO weight percentages (5, 10, 15, 20, and 25%) were generated. The composites are then cured in an oven at 60 °C for a day.

C. Characterization of Ppy-$BaCuO_2$ polymer nanocomposite films:

The prepared Ppy-$BaCuO_2$ polymer nanocomposite films were used for further characterization. The crystalline condition of these films was studied using an X-ray diffractometer (Ultima IV Japan) with CuKα emission (=1.5405) at 40 mA and 40 kV at a scanning speed of 0.02˚/sec. The chemical bonding was analyzed by using FTIR – Perkin Elmer make-model Spectrum RXI spectroscopy. Morphogical properties of the films were obtained using scanning electron microscopic (SEM) (SEM, JSM-6360LV, Japan) operating at 120 kV. Using a programmable Keithley source metre, the (I-V) properties of the films were obtained (Keithley 2636A).

D. Gas Sensing Measurements:

Ammonia (NH_3) is used as probing gas. Resistance is measured with a digital multimeter, and a digital thermometer with an alumel-chromel thermocouple is used to measure temperature of the micro heater fitted with gas sensing measurements were carried out using a gas sensor unit [20]. In our experiments, we first set the oven temperature to a specific value by adding 12.5 V to the furnace to maintain a constant temperature of 150°C, then we measure the resistance of the sensor in the air. A known quantity of Ammonia (NH_3) is injected into the chamber, the sensor's resistance decreases over time, which is recorded. The device is exposed to open air after the bottle is opened once the minimal constant resistance value is obtained. The rise in resistance over time is now being recorded. Under the identical condition for all samples, a similar technique was repeated numerous times (films) [12-13].

III. RESULT AND DISCUSSIONS

FT-Infrared analysis

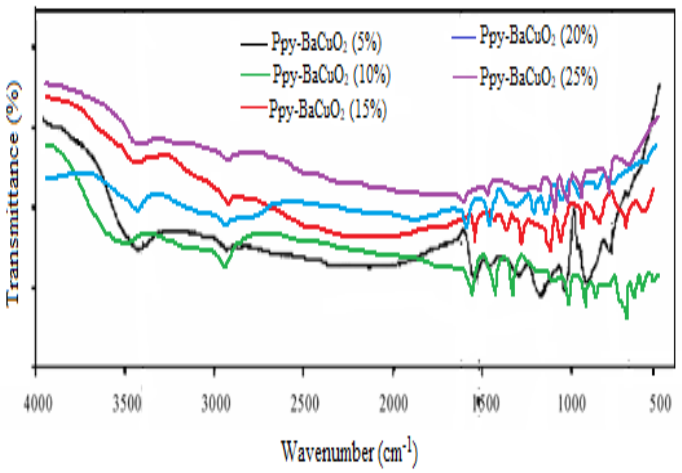

Fig.1. IR spectra of Polypyrrole-$BaCuO_2$ composites thin films

The Fig. 1 shows the FT-Infrared spectra of pure Polypyrrole, and Polypyrrole-$BaCuO_2$ nanoparticle composites loaded with by weight % (5, 10, 15, 20 and 25%). The synthesis of Ppy was confirmed by Fig.1 shows the spectra of bulk PPy. Stretching vibrations of C-C and C=C in the pyrrole ring are assigned to the weak band at 1470 cm^{-1} and the strong band at 1560 cm^{-1}[14]. In the IR spectra, Ppy exhibits pyrrole's distinctive C-H and C-N stretching vibrations at 1051 cm^{-1} and 1202cm^{-1}, respectively [15]. C-H in-plane deformation modes correlate to the absorption at 1317 cm^{-1} [16]. The N-H vibration and out-of-plane ring deformation in polymers may be responsible for the bands seen at 920 cm^{-1} and 677 cm^{-1} [17-18]. Fig.1 indicates that FT-IR spectrum of Polypyrrole Ba- doped CuO nanoparticle components loaded with by weight % (5, 10, 15, 20 and 25%) the peak is strongly attenuated, suggesting that Ppy is applied to each nano particle. The band at 1560 cm^{-1} and 1469cm^{-1} The pyrrole ring has lost its C-C and C=C stretching modes, resulting in the appearance of a broad band at 1485 and 1525cm^{-1} in 20% and 10% content of Ba-doped CuO nanoparticle respectively. The peak was noticed at higher frequencies due to the metal oxide bond from 1319 to 1292, 1205 to 1185 and 1055 to 1046 cm^{-1} with a wide peak at 895 cm^{-1}. Such broad variations are the result of a chemical interaction between $BaCuO_2$ nanoparticles and Ppy. As a result, the conjugation or chain length increases.

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XRD analysis

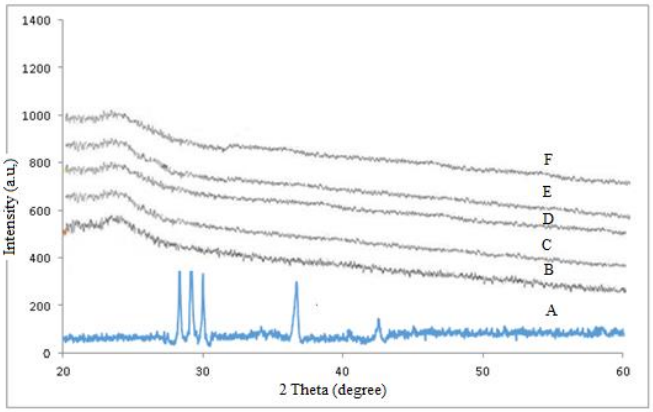


Fig.2: XRD Pattern of $BaCuO_2$ and $BaCuO_2$ doped polypyrrole composite thin films

Fig. 2(B-F) exhibits the usual diffraction patterns seen in X-rays for the Ppy -$BaCuO_2$ composites samples. In the recorded XRD patterns, the detected diffraction peaks are the same as those found in normal $BaCuO_2$ polycrystalline patterns. The peak frequencies of produced powder at 36.36 (2θ) were identical to those of standard data. In our samples, there are no diffraction peaks of Al or another impurity phases, showing that Ba ions would properly replaced within the Cu interstitial sites or sites in the CuO lattice. CuO nano particles developed in the polycrystalline structure after the doping of Ba, as seen in fig 2(A). When comparing the crystallisation of CuO and $BaCuO_2$, the presence of a substantial number of Ba dopants caused lattice instability, which is linked to the stress generated. Aside from the stress issue, when Ba dopants were combined with CuO, the grains grew more easily.

The X-ray diffraction curves of Polypyrrole and its components are shown in Fig.2 (B-F). At under diffraction angles 2θ = 22.500, all patterns have broad peaks, indicating their amorphous nature. The dispersal of the inter planner spacing of the Ppy chains [19] is responsible for the widening of peaks.

Morphology Using SEM

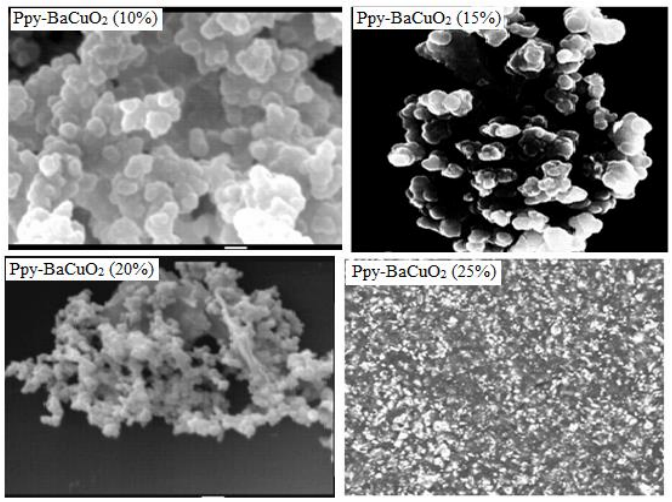
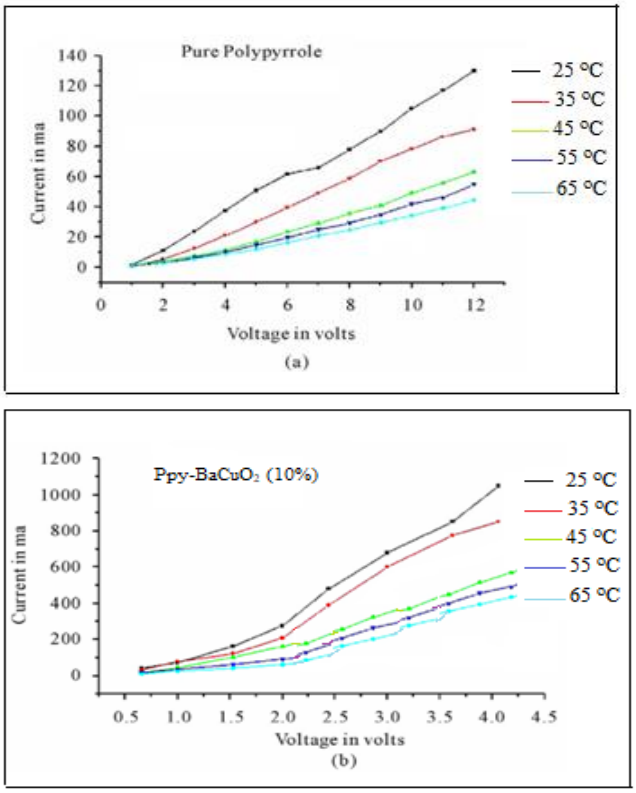


Fig. 3 SEM of $BaCuO_2$ and $BaCuO_2$ doped polypyrrole composite thin films

The chemical and electrochemical morphological aspects of Ppy synthesis have indicated that the progress is typically spherical, yet that this can alter due to dopant molecules. Figure 3 shows model SEM pictures of several Ppy compounds. A globular structure can be observed in all of the photos [20]. Individual granules were practically spherical and packed tightly together. Such spherulites appear to be developing one on top of the other, making enduring shape. The sizes of such spherulites range from 0.3µm to 0.8µm. When dopants were applied during the polymerization with polypyrrole, the granule sizes were observed to be distinct. The average size of $BaCuO_2$ was 0.61µm, with variances ranging from 0.3µm to 0.8µm When $BaCuO_2$ was taken as a dopant, the size of the particle was reduced by 0.30µm. Moreover, the morphological aspect was spongy in nature, making it difficult to differentiate the granules from one another. This indicates the formation of a densely packed structure, which verifies our earlier result based on XRD. When $BaCuO_2$ (25%) was utilised as a dopant, the average globular size was found to be 0.86 µm, which is quite significant in compared to earlier procedure. Such morphological characteristics are expected to be beneficial for gas sensing advantages.

I-V Characteristics



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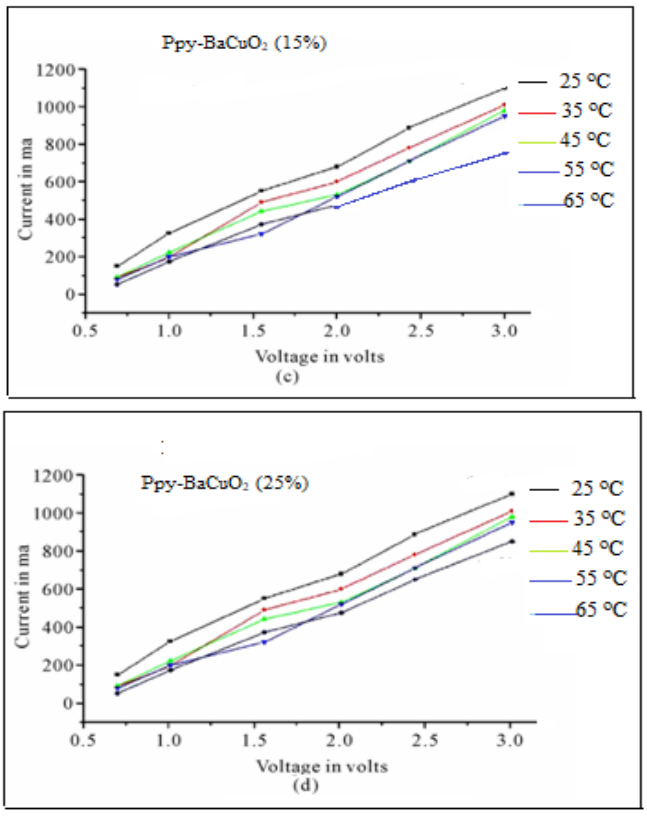

Fig.4. Typical plots of Current vs.Voltage for $BaCuO_2$ doped Ppy nanocomposites thin films

Typical plots of Current vs.Voltage for $BaCuO_2$ doped $FeCl_3$ was used as an oxidant in the synthesis of polypyrrole and with by weight % of $BaCuO_2$ (5, 10, 15, 20 and 25%) as dopants are given in Figure 4. The I-V curve was found to have a nearly linear relationship. The electrical conductivity of polypyrrole was found to enhance when dopants such as by weight % of $BaCuO_2$ (5, 10, 15, 20 and 25%) were used and conductivities were observed in the variation of 10^{-3} S per cm to 10^{-2} S per cm. It should be noted that actual pyrrole behaves more similar an insulator than a semiconductor when doped. The production of polarons and bipolarons by dopant molecules is thought to constitute the mechanism of conduction [21-23]. Top of the valence band and just under the conduction band, additional energy bands arise. The energy gap is narrowed, and the doping causes semiconduction. As a result, increased temperature is projected to result in a rise in energy in the valence band for an electron, causing it to jump to the conduction band, boosting conductivity. However, the current research shows that the materials act more like metals than semiconductors, with conductivity dropping as temperature rises [24]. The vast no. of intermediate energy levels in the energy gap area can induce such behaviour. The doping level in these studies was 25%, which is rather intense and results the overlay of a significant no. of energy levels. As a result, the temperature dependency can be recognized. The conductivities changes at $BaCuO_2$ doped polypyrrole is in the order 25% > 20% > 15% > 10% > 5% > pure by weight % of $BaCuO_2$ as dopants.

Gas Sensor

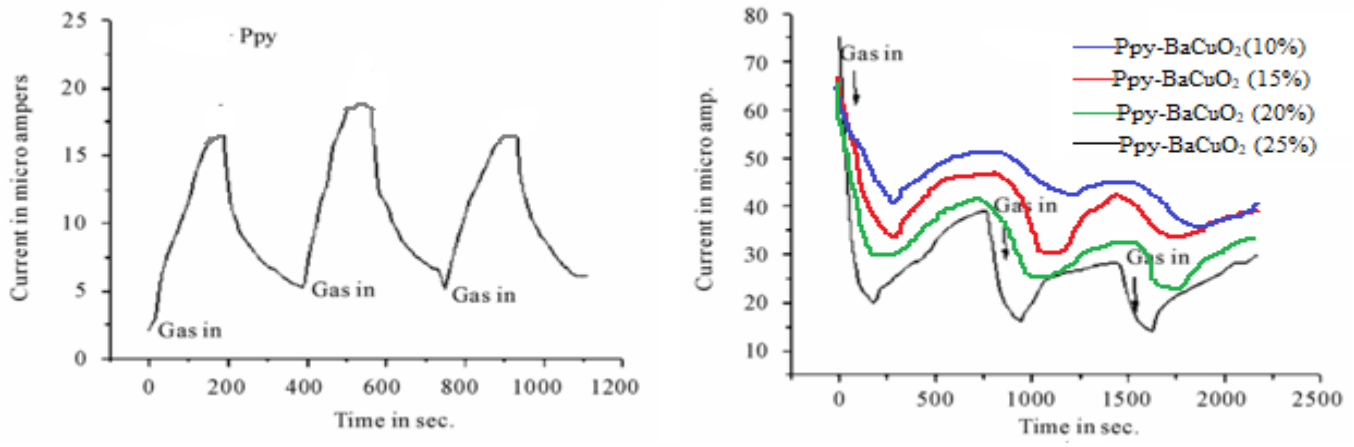

Fig.5 curves of I vs. time for Ppy and Ppy-$BaCuO_2$ nano composite thin films exposed to ammonia gas

The detection of ammonia gas was studied in all of the $BaCuO_2$ doped polypyrrole samples. Figure 5 shows a classical curve of I vs. time for Ppy exposed to ammonia gas. All samples were tested three times to ensure that their absorption and desorption processes were consistent. Fig. 5 shows that current vs time plots for the second and third cycles separate from the 1st cycle. This could be due to the fact that desorption may not be finished within the allotted time. The equation is used to calculate the sensitivity factor.

$$S = \frac{Rg - Ro}{Ro}$$

where Rg and Ro are resistances with gas and without gas (in air) respectively [25-27]. The reaction of pure Ppy and $BaCuO_2$ doped Ppy to ammonia gas was observed to be distinct. During the course of these examinations, it was discovered that when $BaCuO_2$ doped Ppy doped with different weight % of dopants of $BaCuO_2$, decrease in current was noticed when exposing to ammonia gas. These $BaCuO_2$ doped Ppy have a greater electrical conductivity

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than pure polypyrrole, indicating that doping volume and quantity of charge carriers created in the methods are utterly significant. As a result, because there is already a larger charge density, the addition of more charges cannot be produced by ammonia, although reduces the effective charge. As a result, the conductivity of Ppy will drop in this circumstance, as we have seen in our research.

IV. CONCLUSION

Ppy-$BaCuO_2$ polymer nanocomposite thin films were synthesized by chemical oxidation method. The FT-IR spectra of pure polypyrrole, and PPy-BaCuO2 nanoparticle composites enclosed by weight % (5, 10, 15, 20 and 25%). The peak was noticed at higher frequencies due to the metal oxide bond from 1319 to 1292, 1205 to 1185 and 1055 to 1046cm^{-1} with a wide peak at 895 cm^{-1}. Such significant variations are the result of a chemical interaction between $BaCuO_2$ nanoparticles and Ppy. As a result, the conjugation or chain length increases. The XRD curves of polypyrrole and its components are shown at smaller diffraction angles 2θ= 22.500, all patterns have broad peaks, indicating they are amorphous nature. When $BaCuO_2$ (25%) was utilised as a dopant, the mean globular size was observed to be 0.86 µm, which is quite big in compared with another Ppy-$BaCuO_2$ composites. These morphological features are supposed to be useful in gas sensing purposes. The conductivities change of $BaCuO_2$ doped polypyrrole is in the order 25% > 20% > 15% > 10% > 5% > pure by weight % of $BaCuO_2$ as dopants. The response of pure Ppy and $BaCuO_2$ doped Ppy to ammonia gas was observed to be different.

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