Structural, Optical and Electrical Conductivity Studies in Polycarbazole and its Metal Oxide Nano Composites

B. Raghavendra1 · T. Sankarappa1 · Amarkumar Malge1

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Abstract
Polycarbazole (PCz) has been synthesized by chemical oxidation method using APS as an oxidizing agent and PCz/CuO and PCz/Fe2O3 nanocomposites by in situ polymerization method for different wt% of CuO and Fe2O3 at room temperature. XRD patterns confirmed crystalline nature of samples. FTIR indicated strong interaction between PCz and nano fillers. The morphological and optical absorption studies were carried out using SEM and UV–Vis respectively. Addition of CuO or Fe2O3 to PCz decreased its direct and indirect band gaps. However, band gap showed a small change with dopant contents up to 30%. Urbach energy decreased with the addition of dopants. But Urbach energy of the composites increased with increasing dopants content from 10 to 30%. DC conductivity of PCz and its nanocomposites has been measured by following two probe technique in the temperature range 300–423 K. The conductivity of both the nanocomposites is found to be less than the pure PCz and it is found to increase with wt% of CuO or Fe2O3 as the case may be. The activation energy has been determined by fitting Arrhenius expression to the dc conductivity data at high temperature. The activation energy of polycarbazole is determined to be less than that of the composites. In both the composites, activation energy decreased and conductivity increased with the increase of dopant content.

Keywords Polycarbazole · Polymer nano composites · Conductivity · Optical absorption · Band gap

1 Introduction
Polymers are the outstanding invention of the twentieth century which are of long chain structure and generally shows insulating behavior. Conducting polymers are a group of polymers which conduct electricity in pure and doped forms. Conducting polymers are extensively used in manufacturing of sensors, solar cells, diodes, electrochemical super capacitors, memory storage devices, actuators and corrosion protection [1–7].

Recently, the conductivity of many conducting polymers doped with metal oxides has been widely investigated. Among these, polycarbazole (PCz) has been captivated more by its superior properties such as good electrical and thermal, conductivity, high hole mobility, low redox potential and feasible molecular structure and tuning properties [8]. The Ag/PCz has been fabricated by microwave polyol reduction method [9]. Through FTIR and Raman measurements they observed that Ag nanoparticles are enclosed by 3.6 polycarbazole. It was concluded that these composites are advantageous to combine the luminescence behavior of Ag nanoparticles and PCz. DC conductivity of PCz/ZrP has been reported and found that their resistivity was increased on exposure to ammonia, at room temperature [10]. Low dark current in the range of 10−11 A was exhibited by a p-Polycarbazole/n-ZnO hybrid heterojunction diode [11].

The electrical and optical properties of a conducting polymer could be altered by doping metal oxides to it. There have been many studies reported on metal oxide doped polymer nanocomposites with dopants such as CuO, ZnO, Cu2O, MnO2, ZrO2, TiO2 and SnO2 [12–18]. Copper Oxide is blackish brown in color and has monoclinic structure. The manufacturing cost of CuO is very less, shows semiconducting nature and measure a small band gap. Conducting and sensing properties of PANI/CuO nanocomposites have been reported [19]. Temperature dependent conductivity has been studied for polyindole/CuO nanocomposites prepared by sol gel method [20]. Polypyrrole-CuO nano composites were synthesized and studied for optical absorption [21]. It was

1 Department of Physics, Gulbarga University, Kalaburagi 585106, India

✉ T. Sankarappa
sankarappa@rediffmail.com
observed that energy band gap decreases with increase of CuO concentrations in the composites.

Fe$_2$O$_3$ is an inorganic n-type semiconductor shows a non-toxic behavior, which can be abundantly obtained in nature. Fe$_2$O$_3$ is considered as a good electrode material used for constructing lithium ion batteries. Polypyrrole/Fe$_2$O$_3$ nanocomposites have been studied thoroughly for conductivity [22]. It was noted there were variations in both ac and dc conductivity for different concentration of Fe2O3.

It is known that the conjugated conducting polymers have the potential to replace inorganic semiconductors in the development of low-cost electronic, optoelectronic devices and gas sensors. Polycarbazole (PCz) belongs to relatively new conducting polymer groups having good thermal stability, electrochemical and photo sensitivity. It’s electrically conducting form can be easily synthesized by the electrochemical polymerization route. Among the metal oxides normally used for preparing polymer composites, CuO is most suited as it is of low cost and possesses good electrochemical properties which make it useful for optical, electrical and gas sensing applications. Fe$_2$O$_3$ is considered to be a good electrode material used in lithium ion batteries. There are not many reports available in the literature on PCz and its metal oxide composites. In view of this, we synthesized and investigated polycarbazole, PCz/CuO and PCz/Fe$_2$O$_3$ nanocomposites for structural, morphological, optical and electrical properties. Insight into these properties can enable one to investigate and try them for the applications of electrical and optical and gas sensing.

2 Experimental

2.1 Sample Preparation

Present samples were synthesized by chemical oxidative polymerization method using the raw materials of high purity (more than 95%) such as Carbazole (Sigma), Ammonium persulphate (SD-Fine), Acetonitrile (MERCK), Copper Oxide (Himedia), Ferric oxide (Himedia) and double distilled water (NICE).

2.1.1 Synthesis of PCz

These chemicals have been taken as such for synthesis without any specific characterization. Monomer solution was prepared by dissolving 3.34 gm of Carbazole in 50 ml of acetonitrile. The APS (oxidant) solution was prepared by dissolving 9.12 gms of APS in 50 ml of water. Molar ratio of 1:2 was maintained between monomer and oxidant. The APS solution was added slowly (drop wise) to the carbazole solution over a period of 30 min. The mixture was constantly stirred for 24 h at room temperature and obtained dark green solution. The precipitate was filtered and washed several times with deionised water and methanola and kept the yield for annealing at 150 C.

2.1.2 Synthesis of PCz/CuO AND PCz/Fe$_2$O$_3$ Composites

The nanocomposites were prepared by in situ oxidative polymerization of carbazole by adding different amounts of CuO using APS as oxidizing agent. Carbazole (3.34 gms) was dissolved in acetonitrile (50 ml). CuO (10 wt%) nanoparticles was added to monomer solution under vigorous stirring. APS solution (9.12 gms in 50 ml of water) was added drop wise to the above solution over a period of 15 min. The entire solution was stirred for 24 h and the color of the solution turned to dark green. The precipitate was washed several times with deionised water and methanol successively, filtered and then dried. PCz/Fe$_2$O$_3$ nanocomposites of different wt% of Fe$_2$O$_3$ were synthesized by following the same procedure. The different concentrations of CuO and Fe$_2$O$_3$ (10, 20, 30 wt%) were prepared and labeled as PCu10, PCu20, PCu30 and PFO10, PFO20 and PFO30 respectively.

2.2 Measurements

The powder XRD experiments were performed on all the samples using Cu-Kα radiation of wavelength 1.5405 Å in a Rigaku Ultima IV diffractometer. The well ground samples were spread on a quartz glass plate and it was mounted in the X-ray diffractometer for x-ray scan. The current of 30 mV and voltage of 40 kV was used to generate X-rays. X-rays were scanned for the range from 10 to 80. Scanning rate of 4°/minute was maintained. The crystallite size, D was determined from XRD patterns using Debye Scherer’s formula showed in Eq. (1) and micro strain, ε using Eq. (2) [25],

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

\[ \varepsilon = \frac{\beta}{4 \tan \theta} \]

where, K is a constant called shape factor equal to 0.9 for spherical shaped particles [24], λ is wavelength of X-ray (~1.5406 Å), β is full width half maximum and θ position of the peak.

FTIR spectra of the present samples were recorded in a Shimadzu (Prestige-21) spectrophotometer in the wave number range 400–4000 cm$^{-1}$ of 4 cm$^{-1}$, using KBr pelleting method. For this, the sample and the dry KBr were mixed in 1:10 ratio in a glass mortar and grinded. The mixture was then made into a circular disk by pressing in
a hydraulic pelleting machine under a pressure of 1 ton. The disk was then held in the instrument beam for spectroscopic examination. Optical absorption studies of the present samples were carried out in a Shimadzu UV-1800 spectrophotometer in the wavelength range 190–900 nm. The solution form of the samples was prepared by dissolving 1 mg of sample in 10 ml of Acetonitrile. The first scan was performed without the sample in the beam path and then the solution was poured into a small container (holder) and kept in the beam path. The samples were scanned and absorbance was measured.

**Table 1** Crystallite size, D average crystallite size and Micro strain, ε of PCz, PCuO and PFO composites

| Sl no | Sample | 2θ (Degrees) | FWHM (β) | Crystallite size (nm) | Average crystallite size (nm) | Micro strain (ε) |
|-------|--------|--------------|----------|-----------------------|-------------------------------|-----------------|
| 1     | PCz    | 20.04        | 0.33     | 24.07                 | 24.07                         | 0.47            |
| 2     | CuO    | 35.60        | 0.27     | 29.42                 | 29.42                         |                 |
| 3     | Fe₂O₃  | 33.35        | 0.31     | 25.62                 | 25.62                         |                 |
| 4     | PCu10  | 19.43        | 0.30     | 26.51                 | 34.14                         | 0.44            |
| 5     | PCu20  | 19.53        | 0.25     | 31.77                 | 34.14                         | 0.36            |
| 6     | PCu30  | 19.52        | 0.18     | 44.15                 | 34.14                         | 0.26            |
| 7     | PFO10  | 19.49        | 0.26     | 30.06                 | 42.89                         | 0.38            |
| 8     | PFO20  | 19.51        | 0.19     | 41.81                 | 42.89                         | 0.27            |
| 9     | PFO30  | 19.47        | 0.14     | 56.82                 | 42.89                         | 0.20            |
estimated using stored reference data and the accumulated in the computer.

The optical absorption gives information about energy band gap and electronic transitions. Optical energy band gaps can be determined using Mott-Davis-Tauc’s equation [28].

\[
\frac{(\alpha h \nu)^1}{n} = \frac{2.303}{d} = B(h \nu - E_g)
\]

where, \(\alpha\) is the absorption coefficient, \(B\) the absorption constant, \(h \nu\) the energy of the photon, \(\nu\) the frequency of radiation, \(E_g\) the optical energy gap and \(d\) the sample thickness and \(h\) the Planck’s constant. The exponent \((1/n)\) represents different electronic transitions and it takes values \(1/2\), \(2\), \(3/2\) and \(3\) corresponding to allowed direct, indirect, forbidden direct and forbidden indirect transitions respectively. The direct and indirect energy gaps are determined from the transition of electrons from valance band to conduction band when photons interact with them in the valance band.

**Table 2** Assignment of bands to different functional groups in FTIR spectra of PCz, PCuo and PFO composites

| S.No | FTIR bands in PCz (cm\(^{-1}\)) | FTIR bands in PCz/CuO composites (cm\(^{-1}\)) | FTIR bands in PCz/Fe\(_2\)O\(_3\) composites (cm\(^{-1}\)) | Assignment of bands |
|------|---------------------------------|-----------------------------------------------|-------------------------------------------------|-------------------|
| 1    | 562–610                         | 602 to 610                                    | 562–610                                         | Fe–O stretching vibratio mode [23] |
| 2    | 602 to 610                       | 717 to 723                                    | 720                                             | Vibration of Cu–O bond [21] |
| 3    | 726                              | 727                                          | 720                                             | Ring deformation of substituted aromatic structure [26] |
| 4    | 812                              | 812                                          | 814                                             | C-H deformation in tri substituted benzene ring [27] |
| 5    | 918                              | 918                                          | 918                                             | \(=\)CH out of plane vibrations [21] |
| 6    | 1227                             | 1227                                         | 1232                                            | C= N stretching [27] |
| 7    | 1316                             | 1316                                         | 1316                                            | C-H out of plane bending vibration of aromatic ring [27] |
| 8    | 1444                             | 1444                                         | 1444                                            | Ring stretching vibration of carbazole moiety [27] |
| 9    | 1598                             | 1598                                         | 1598                                            | stretching mode of aromatic alkene [25] |
| 10   | 3415                             | 3415–3419                                    | 3415–3420                                       | Stretching of N–H bond [25] |
Morphology of PCz and the composites has been studied using CARLZEISS scanning electron microscope. A working voltage of 5 kV and magnification of 1.00 KX has been used. Images were inspected on the computer screen to understand them qualitatively.

The samples were pelletized in a hydraulic press by applying the pressure of 20 kg/cm². The pellets all the samples were in circular shape and their thickness was in the range of 2.5 mm to 4.5 mm. To get better electrical contact between the probes and the sample, bottom and top surfaces of the pellet was painted with silver. The dc conductivity measurements were carried out by following a two probe method by applying a constant voltage of 5 V across the pellet in the temperature range from 300 to 423 K. Current was measured using a nano ammeter. The electrical resistivity, ρ was estimated by ρ = R(A/t), where R = (V/I), A is the area of bottom/top surface area of the pellet and t the thickness of pellet. Conductivity, σ has been determined using the expression, σ = 1/ρ, within the accuracy of 2%.

It is known that four probe method is best suited for measuring low resistivity so that the problem of contact resistance can be avoided. Due to unavailability of four probe setup we could not use four point method. The present samples are powders, not wires or sheets. So, making four point contact to the sample is tricky and difficult. There were large number of previous works wherein two probe method was used to measure electrical conductivity of polymers [12, 19].

3 Results and Discussion

3.1 XRD

The crystalline structure of pure PCz and composites PCz/CuO and PCz/Fe₂O₃ were investigated from XRD patterns. The XRD patterns of the present samples are shown in the below Fig. 1. Some diffraction peaks corresponding to different crystalline planes can be seen. The sharp peaks

Fig. 3 SEM morphologies of PCz, PCu10 and PFO10
at 35.77°, 38.91°, 48.82°, 58.54°, 61.62°, 66.50°, 68.18°, 72.59°, 75.35° correspond to (0 0 2), (2 0 0), (2 0 2), (0 2 0), (2 0 2), (2 2 0), (3 1 1), (0 0 4) planes of monoclinic structure of CuO. Peaks at 24.19°, 33.15°, 35.77°, 40.96°, 49.68°, 54.32°, 62.47°, 63.96° correspond to (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (2 1 4), (3 0 0) planes of rhombohedral structure of Fe2O3. The CuO and Fe2O3 patterns are found to be consistent with JCPDS file Nos. 48–1548 and 89–8104 respectively [19, 23]. The peaks at 19.03°, 20.01°, 21.16°, 23.16°, 28.12° correspond the planes (2 0 − 1), (1 2 − 1), (2 2 0), (0 1 2), (2 1 0) of polycarbazole [24]. The increase in peak intensity with increasing concentration of CuO and Fe2O3 confirms interaction of dopants with PCz. The crystallinity of the composites enhanced due to increased concentration of nano sized dopants.

The prominent peak for each sample was considered for determining crystallite size and micro strain. The obtained values of crystallite size, average crystallite size and micro strain of the samples are tabulated in Table 1. It can observed that the crystallite size of PCz is less compared to composites, crystallite size is increasing and micro strain is decreasing with wt% of dopants which confirms encapsulation of polycarbazole on the dopant particles. These are in qualitative agreement with the literature on PCz/SnO2 [24].

### 3.2 FTIR Analysis

The FTIR has been analyzed to know different functional groups developed in the composites due to interaction between constituents such as PCz and CuO and, PCz and Fe2O3. The spectra of the present nanocomposites are shown in the Fig. 2. The IR bands at 726 cm−1 and 812 cm−1 are due to C-H deformation of di-substituted and tri-substituted benzene ring of PCz respectively [26, 27]. A sharp band around 3415 cm−1 refers to stretching of the N–H bond in PCz. The change in intensity and shifting of 3415 cm−1 band evidenced the formation of bond between NH group of PCz and CuO and, Fe2O3 [25]. The presence of the stretching band at 1227 cm−1 is attributed to C=N and the peak at 1316 cm−1 is attributed to C-H out of plane bending vibration of aromatic ring. The sharp band around 1444 cm−1 may be due to ring stretching vibration of carbazole [27]. The bands at 918 cm−1 and 1598 cm−1 are assigned to =CH out of plane and stretching mode of aromatic alkenes respectively [21, 25]. A strong absorption band at 562 cm−1 and at 602 cm−1 in the composites confirms incorporation of Cu–O and Fe–O vibrational modes respectively [21, 23]. The assignment of bands of different functional groups are tabulated in Table 2.
Fig. 5 Tauc’s plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for direct band gap determination

Fig. 6 Tauc’s plots of $(\alpha h\nu)^2$ versus $h\nu$ for indirect band gap determination
Table 3 Optical Band gap energy (direct and indirect) and Urbach energy values for PCz, PCuo and PFO composites

| Sl no | Sample | Direct band gap $E_g$ (eV) | Indirect band gap $E_g$ (eV) | Urbach energy $E_u$ (eV) |
|-------|--------|---------------------------|-----------------------------|-------------------------|
| 1     | PURE PCz | 3.32                      | 3.42                        | 0.32                    |
| 2     | PCu10  | 3.47                      | 3.54                        | 0.30                    |
| 3     | PCu20  | 3.48                      | 3.53                        | 0.31                    |
| 4     | PCu30  | 3.46                      | 3.52                        | 0.32                    |
| 5     | PFO10  | 3.49                      | 3.53                        | 0.30                    |
| 6     | PFO20  | 3.47                      | 3.52                        | 0.32                    |
| 7     | PFO30  | 3.46                      | 3.51                        | 0.33                    |

3.3 Morphology

Figure 3 shows typical SEM images of PCz, PCu10 and PFO10 nanocomposites. It is evident from the images that the polycarbazole has homogeneous surface morphology with nodular nature and the particles are agglomerate. It can be observed from the images of PCu10 and PFO10 nanocomposites that there are morphological changes occurring upon adding the CuO/Fe$_2$O$_3$ nanoparticles. The added nanofillers lead to branching of polymer chain in the polycarbazole and that in turn created network like structure in composites. Similar results were obtained for samples PCU20, PCU30, PFO10 and PFO30.

3.4 UV–Vis Absorption Analysis

Figure 4a and b depicts optical absorption spectra of the samples PCz, PCu10, PCu20, PCu30, PFO10, PFO20 and PFO30. A broad band is observed at 279 nm in pure polycarbazole is assigned to bonding and antibonding ($\pi-\pi^*$) transition of the benzoid ring and small peak around 347 nm is corresponding to polaronic energy level ($n-\pi^*$) transition of the quinoid ring. The polaronic energy level is created by the formation of defects during polymerization process [24, 26]. It is observed that the peaks are slightly shifted to blue end about 4 nm for CuO composites and to 8 nm for Fe$_2$O$_3$ composites of spectrum and also there is variation in the intensity with different concentration of CuO and Fe$_2$O$_3$. This is because CuO or Fe$_2$O$_3$ nanoparticles absorbs partly incident radiation by their free electrons and due to the strong interaction between polymer and dopant nanoparticles. The blue shift on a small scale with increase in CuO wt% is in agreement with the reports, PCz/SnO$_2$ [25].

The Tauc’s plots for direct and indirect transitions were made and tangents to the band edges were extrapolated on to the $h\nu$-axis. The intersecting values on $h\nu$-axis gave band gap values corresponding to direct or indirect transitions as the case may be. The typical plots of direct band gap for one sample in each series and for pure PCz are shown in Fig. 5.

![Plots of ln(α) versus hv for PCz, PCu10 and PFO10 composites for Urbach energy determination](image-url)
and for indirect band gap in Fig. 6. To save space, Tauc’s plots for all the corresponding are not shown in the Fig. 5 & 6.

The results tabulated in Table 3 revealed that the intended direct and indirect band gap values of pure PCz were 3.32 eV and 3.42 eV respectively. For PCu10, direct and indirect gaps are found to be 3.47 eV and 3.54 eV respectively. It implies that band gap values increases on doping PCz with CuO. Similarly, for PFO10, direct and indirect gaps are 3.49 eV and 3.53 eV. These results are also suggest that band gap of PCz increases when doped with Fe2O3. This may be due to strong interaction between the polymer matrix and dopant oxides. Increase of CuO or Fe2O3 from 10 to 30 wt% decreases band gaps slightly. Similar nature of results were reported for PCz/SnO2 and PVA/CuO [24, 28].

The Urbach energy (Eu) was determined by plotting ln(α) versus hν as depicted in Fig. 7. Urbach energy (Eu) of pure PCz is determined to be 0.325 eV [Table 3]. This value decreased to 0.307 eV when 10 wt% of CuO or Fe2O3 are doped to PCz. Since Urbach energy is a measure of defects in the sample, present results indicate that samples improve their quality in terms of defects when they were doped with 10 wt% of dopant oxides. On increasing dopants beyond 10 wt% Urbach energy increases. This reveals that higher amounts of dopant oxides increases concentration of structural defects in the samples. Similar results were quoted for PVA/CuO composites [28].

\[ \sigma = \sigma_0 \exp \left( \frac{E_a}{k_B T} \right) \]

where, \( \sigma_0 \) is the pre-exponential factor, \( E_a \) the activation energy and \( k_B \) the Boltzman constant.

Figures 8 and 9 shows the plots of ln(σ) versus (1/T) for pure PCz and PCuO and PFO composites respectively. The linear lines were fit to the data at higher temperatures and the obtained slopes of the fits were used to determine the activation energy \( E_a \). Figure 10 shows activation energy \( E_a \) and σ at 400 K versus wt% of CuO/Fe2O3 composites, it can be seen that activation energy \( E_a \) decreased and conductivity increased with increase of dopant concentration and, it may be due to the decrease in the scattering rate of polarons with increase of CuO/Fe2O3 concentration. The conductivity and activation energy values of PCz, PCz/CuO and PCz/Fe2O3 nanocomposites at 350 K and 400 K are tabulated in Table 4. To emphasize conductivity behavior with filler content its value at two different temperatures are shown in Table 4. Similar kind of behavior in \( E_a \) and σ has been observed in reference [29] for PVA/CuO composites and noticed enhancement in conductivity and reduced activation energy in PVA doped CuO. Increase in conductivity with TiO2 content in PCz/TiO2 nanocomposites has been noted [30]. Conductivity of polyindole, polycarbazole and their derivatives were compared and found that polycarbazole had higher conductivity than polyindole [31].

4 Conclusions

In the present work, polycarbazole has been synthesized via chemical oxidation method and the composites, PCz/CuO and PCz/Fe2O3 by in situ polymerization technique. The samples were characterized by XRD, FTIR, SEM and UV–Vis. The results revealed that the composites are influenced by the loaded CuO/Fe2O3 nanofillers. Crystalline nature of the materials and strong interaction between PCz and dopants are confirmed by XRD and FTIR respectively. SEM images showed a remarkable morphological distinction
between the polycarbazole and the composites. The optical absorption bands showed blue shifts in the peak positions which reveals inter molecular interactions between the added nanofillers and the polymer matrix. The direct and indirect band gaps were determined by Mott-Davis Tauc equation and found that the band gap of the composites are higher than the pure polycarbazole and the band gaps of the composites showed a small change with dopant content up to

Fig. 9  Plots of ln(σ) versus (1/T) for PCuO and PFO composites. Solid lines are the linear fits to data at high temperature
wt 30% with increase in wt% of the fillers. Conductivity of both PCz and the composites increased with increase in temperature indicating semiconducting nature. Conductivity of the composites increased and activation decreased with wt% of CuO/Fe$_2$O$_3$ content. The present study of composites is limited to the doping level up to 30% of metal oxides and this can be increased up to 50 wt% and study can be carried out. The data collected will enable to propose these composites for suitable applications of electrical and optoelectronic devices. Gas sensing applications can also be carried out on these samples. For the first time PCz and its metal oxides doped composites have been thoroughly investigated for structural, morphological, optical and electrical conductivities.

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