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Conduction Mechanisms in Polypyrrole-Copper Nanocomposites

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By mixing independently synthesized polypyrole and copper nanoparticles in different proportions, nanocomposites were prepared. Bulk and surface structures were probed by X-ray diffraction and Scanning electron microscopes. DC resistivity with temperature as a variable of all the composites has been investigated. Conductivity has been calculated using resistivity and found it to be of the order 10^{-4} ($\Omega^{-1}m^{-1}$), which is greater by one order of magnitude than that reported for polypyrole nanoparticles. Temperature behaviour of conductivity in all the samples revealed semiconducting nature. By applying Mott's theory of small polaron hopping, activation energy for conductivity at high temperature has been determined. Activation energy is found to be increasing with increase in copper content in the composites. Using data deviated from small polaron model, the density of states at Fermi level is calculated by employing the theory of variable range hopping of polarons due to Mott. It is for the first time that PPy-Cu nanocomposites have been probed for structural and temperature dependence of conductivity and conduction mechanisms operated in these composites in different temperature regions have been understood.

Keywords: PPy-Cu nanocomposites, Structure, Polaron hopping, Density of states.

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1. INTRODUCTION

Conducting polymers are the most attractive materials for research due to their attractive applications. The unique properties of nanoparticles of metals and conducting polymers lead to an increasing interest and motivation in the synthesis of nanocomposite materials [1, 2]. The metal nanoparticles such as copper have applications in catalytic activities and in various electronic components [3]. The composites made of metal nanoparticles and an organic semiconductor is expected to exhibit a good level of conductivity as well as tunable physical and chemical properties [4]. Of these, the composites made of polypyrrole (PPy) and copper or silver nanoparticles are most popular. The size control of PPy nanoparticles has been investigated and reported that PPy nanoparticles can be effectively dispersed due to large surface area and they exhibit sizable conductivity [5-7].

Also, Copper nanoparticles are attracted considerable attention as copper is an inexpensive and good conductive material. Copper nanoparticles of sizes in the range from 40 nm to 50 nm were synthesized and using them a well dispersed conductive ink with low viscosity has been prepared. The ink-jet printed copper pattern exhibited conductivity of 5.8×10^6 $\Omega^{-1}m^{-1}$ [8]. The band gap energy of copper nanoparticles was determined using photoluminescence spectrum of aged copper nanoparticles [9].

The electrical conductivity of PPy-Cu nanocomposites was measured by four probe technique and the value was 4.13 $\Omega^{-1}m^{-1}$ [10] and conductivity increased with Copper nanoparticles content and temperature [11]. Nano composites of polypyrrole coating Copper Sulfide (CuS) were synthesised by an in situ chemical oxidative polymerization. The electrical conductivity increased with increase in number of CuS nanoparticles in the polymer matrix. Also, this system exhibited improved stability and enhanced conductivity [12].

Here, the results on structural and electrical studies of Polypyrrole-Copper (PPy-Cu) composite nanoparticles are presented. The conductivity data has been viewed in light of Mott's polaron hopping models [13].

2. EXPERIMENTAL

Analytical grade Pyrrole, Ammonium Peroxidisulphate, Methanol, Copper sulphate (penta hydrated) and Sodium Borohydride were used in the preparation of PPy nanoparticles and Copper nanoparticles. Preparation of PPy nanoparticles was carried out at a temperature of 277 K. Aqueous solution of Pyrrole was prepared and stirred for 30 minutes to attain homogeneity. Aqueous Ammonium persulphate (APS) solution has been added drop wise to the PPy solution. After addition of few drops of APS, the solution turned in to green indicating the formation of Polypyrrole nanoparticles in the colloidal solution. Further addition of APS, the solution became black. The reaction has been carried out for eight hours. The colloidal solution was filtered and washed with double distilled water, methanol and acetone several times to remove unreacted pyrrole and ammonia. The powder was collected, dried and grinded [14].

Copper nanoparticles were prepared by chemical reduction method in which ice cooled aqueous solution of sodium borohydride ($NaBH_4$) was added drop wise to aqueous solution of Copper sulphate ($CuSO_4 \cdot 5H_2O$). During the process of reaction the solution was stirred vigorously. The solution was filtered, washed with distilled water and acetone several times. The collected powder was dried and grinded.

Polypyrrole-Copper (PPy-Cu) nanocomposites were made by mixing independently prepared Polypyrrole and Copper nanoparticles in different amounts defined as $(PPy)_{100-x}(Cu)_x$, where $x = 10$ %, 20 %, 30 %, 40 % and 50 % and are labeled as PPy-CU1, PPy-CU2, PPy-CU3, PPy-CU4 and PPy-CU5 respectively. Powder

XRD studies were carried out on the prepared composite nanoparticles using X-pert PRO X-Ray Diffractometer. The samples were subjected to SEM studies in ZEISS, EVO18-Special Edition Scanning Electron Microscope. Temperature dependence of electrical conductivity has been measured in the range from 300 K to 550 K by following two point method. A constant voltage (V) of 5 Volts has been applied across two sides Silver painted pellet of PPy-Cu composite nanoparticles. The current, (I) passing through the pellet has been measured using a picoammeter. Resistivity (ρ) has been determined using the expression [14],

$$\rho = \left(\frac{V}{I}\right)\left(\frac{A}{l}\right), \quad (1)$$

where A is surface area and l the thickness of the pellet. Conductivity σ has been worked out to be the reciprocal of ρ.

3. RESULTS AND DISCUSSIONS

3.1 X-Ray diffraction

XRD pattern recorded for pure Copper nanoparticles using Cukα ($\lambda = 1.5418$ Å) radiation is shown in Fig. 1. These XRD patterns were recorded after one month after the synthesis. In the XRD pattern peaks appearing at $2\theta = 38.41°$ and 48.73° corresponds to diffraction from (111) and (200) planes of pure copper

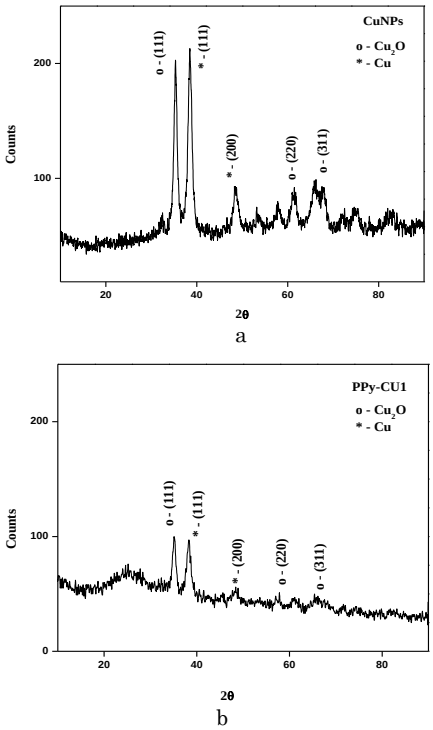

Fig. 1 – XRD patterns for (a) Pure Cu nanoparticles and (b) PPy-CU1 nanocomposites

(JCPDS No. 04-0836). In addition to these two peaks, there are three more peaks at $2\theta = 35.53°$, 61.6° and 66.13° and they correspond to the (111), (220) and (311) planes of Cu_2O [15]. The XRD results confirm the presence of both copper and cuprous oxide in the sample of pure copper nanoparticles and PPy-Cu nanocomposites. It is clear from (*hkl*) indexing that composites are in FCC structure. Peak widths were used to estimate grain size using the Scherrer equation and they are mentioned in Table 1. The particle sizes obtained are in the range of 4 nm to 7 nm.

Table 1 – Peak indexing, Inter planar distance, D and particle sizes

System	2θ	*hkl* indices	D, (Å)	Particle size, (nm)
Cu nps	35.53	(111)	1.63	7
	38.41	(111)	1.52	6
	48.73	(200)	1.21	5
	61.61	(220)	0.98	4
	66.13	(311)	0.92	4

A typical XRD pattern recorded for PPy-CU1 is shown in Fig. 1b. Remaining PPy-CU nanocomposites produced similar patterns. The number of peaks and peak positions were observed to be same for all the five composites. Peak positions noted for composites are exactly the same as Cu nanoparticles. The observed planes of Cu nanoparticles are in good agreement with the reported values [9]. A broad hump is observed at low angle scattering similar to that observed in ref [16] showing the existence of Cu in the PPy-Cu composites. From XRD pattern it is clear that Cu nanoparticles got oxidized and some of them became Cu_2O.

3.2 SEM

SEM images of Cu and PPy-Cu nanoparticles are shown in Fig. 2a and b respectively. These images show Copper nanoparticles to be mostly spherical in nature and agglomerated.

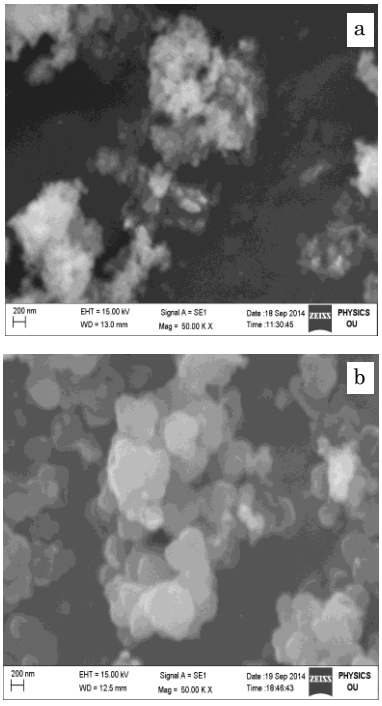

Fig. 2 – SEM images of (a) Pure Copper nanoparticles (b) PPy-CU1 nanocomposites

In Fig. 2b, it can be seen the existence of two types of grains, they could be that of PPy and Cu nanoparticles as some are less bright and some are more bright. Larger agglomeration of particles can be observed in Fig. 2b than in Fig. 2a. Grain sizes are noted to be less than 50 nm for both the type of grains.

3.3 Electrical Conductivity

DC resistivity (ρ) of all the PPy-CU nanocomposites has been measured for temperatures in the range from 300 K to 550 K. Conductivity ($\sigma = 1 / \rho$) was estimated from resistivity. Conductivity variation with temperature for PPy-CU1 shown in Fig. 3. It can be seen that conductivity increases with increase in temperature which reveal the semi conducting type of behavior. Similar nature of variation of conductivity with temperature has been observed for the remaining samples of the present series. The measured conductivity of the PPy-CU nanocomposites is in the order of 10^{-4} ($\Omega^{-1}m^{-1}$), which is an order of magni tude higher than that measured for pure PPy nanoparticles [14]. This indicates that addition of Cu nanoparticles to the PPy nanoparticles matrix enhances the conductivity level.

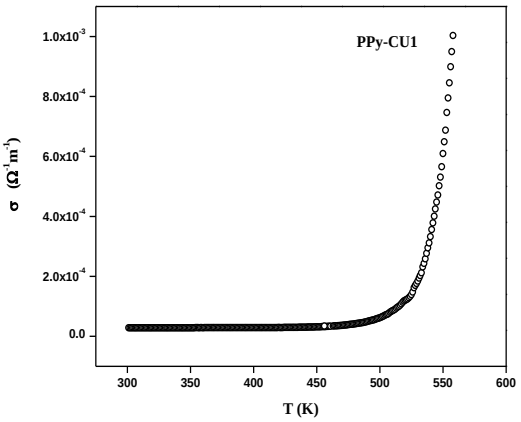

Fig. 3 – Temperature dependence of electrical conductivity of PPy-CU1 nanocomposite

The temperature response of conductivity of the composites has been fit to conductivity expression due to Mott derived for Small polaron hopping (SPH) in noncrystalline semiconductors. It can be noted that in the absence of a good quantitative theory for explaining conduction mechanism in polymers and that the present PPy-CU nanocomposites behaved like semiconductors, SPH model has been employed. According to this model, the conductivity in the non-adiabatic region is given by [13].

$$\sigma = \frac{\sigma_0}{T} \exp\left\{-\frac{E_a}{K_B T}\right\} \qquad (2)$$

Where σ_0 is the pre exponential factor and E_a the activation energy for small polaron hopping. The plots of $\ln(\sigma T)$ versus $(1 / T)$ were made as per Eqn. (2) and shown in Fig. 4a. The linear lines were fit to the data in the high temperature region where the data appeared linear. The slopes were used to determine the activation energy, E_a.

Variation of activation energy E_a, and conductivity at 525 K as a function of weight percent of Cu in PPy-Cu composites are plotted and shown in Fig. 5. From

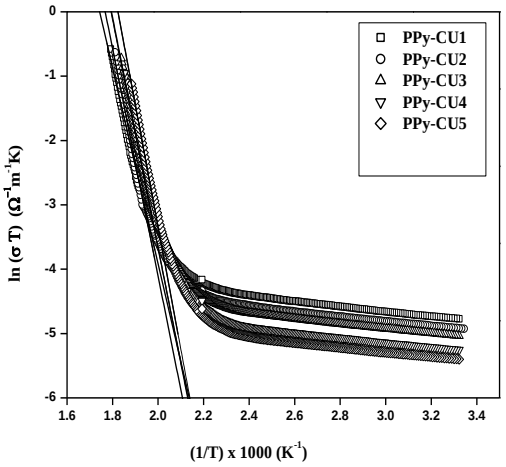

Fig. 4 – The plots of $\ln(\sigma T)$ versus $(1 / T)$ as per SPH model. Solid lines are the linear lines fit through data in high temperature region

the figure, it is seen that activation energy (E_a) and conductivity (σ) both increases with increase of weight percentage of Cu nanoparticles. It is interesting to note that measured conductivity of all the five composites is greater than that reported for pure PPy nanoparticles reported elsewhere [14]. However, increase of weight percent of Cu lead to increase in activation energy and increase in conductivity as well. This suggests that addition of Cu nanoparticles to PPy not only increases conductivity but also increases polaron scattering with polymer matrix and other polarons.

Variation of activation energy E_a, and conductivity at 525 K with of weight percent of Cu in PPy-Cu composites are plotted and shown in Fig. 5. From the figure, it is seen that activation energy (E_a) and conductivity (σ) both increase with weight percent of Cu nanoparticles. It is interesting to note that measured conductivity of all the five composites is greater than that reported for pure PPy nanoparticles reported elsewhere [14]. However, increase of weight percent of Cu lead to increase in activation energy and increase in conductivity as well. This suggests that addition of Cu nanoparticles to PPy not only increases conductivity but also increases polaron scattering with polymer matrix and other polarons.

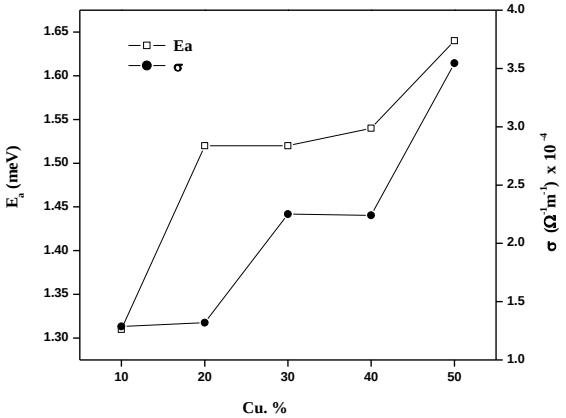

Fig. 5 – Variation of conductivity at 525 K and activetion energy with weight percentages of Cu in PPy

The data deviated from SPH model has been fit to

Mott's VRH model. Mott's VRH has already been used in interpreting conductivity data of polypyrrole and polythiophene [17, 18]. According to this model conductivity is given by

$$\sigma = A\exp\left\{-BT^{-\frac{1}{4}}\right\} \quad (3)$$

Where $A = 4\left[\frac{2\alpha^3}{9\pi k_B N(E_F)}\right]^{\frac{1}{4}}$ and

$$B = \left[\frac{e^2}{2(8\pi)^{\frac{1}{2}}}\right]\upsilon_0\left[\frac{N(E_F)}{\alpha k_B T}\right]^{\frac{1}{2}}$$

Here, $N(E_F)$ refers to density of states at Fermi level, υ_0 is the phonon frequency (10^{13} Hz) and $\alpha \approx 1.2$ Å (Size of the monomer unit) [19]. The plots of ln(σ) versus ($T^{-1/4}$) as per Eqn. (3) for the data deviated from SPH model are shown in Fig. 6. The linear lines were fit through the data. It can be noted that still some data corresponding to further lower temperature has deviated from Mott's VRH model fit.

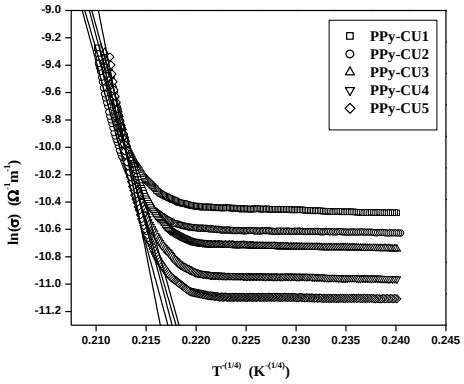

Fig. 6 – Plots of ln(σ) versus ($T^{-1/4}$) as per Mott's (VRH) model. Solid lines are the linear lines fit through data in high temperature region

Density of states, $N(E_F)$, were determined using slope and recorded in Table 2. The $N(E_F)$ are of the order of 10^{28} eV^{-1}m^{-3}. We could not compare the presently obtained $N(E_F)$ values with literature as no PPy composites mixed with copper nanoparticles were ever reported for conduction mechanism. However, These $N(E_F)$ are found to be more than the values reported for semiconducting oxide glasses [20, 21].

Table 2 – Density of states at Fermi level, $N(E_F)$ for PPy-Cu nanocomposites

Systems	$N(E_F)$ (eV^{-1}m^{-3}), $\times 10^{28}$
PPy-CU1	5.8
PPy-CU2	4.33
PPy-CU3	4.61
PPy-CU4	3.61
PPy-CU5	0.93

4. CONCLUSIONS

Polypyrrole and Copper nanoparticles have been synthesised at 277 K by chemical route. Nanocomposites were synthesised by mixing of Polypyrrole and Copper nanoparticles in different weight percentages. XRD patterns indicated the presence of Cu and Cu_2O phases in both copper nanoparticles and PPy-Cu nanocomposites. SEM images showed agglomeration of nanoparticles. Temperature variation of dc resistivity has been investigated and it indicated semiconducting nature. Conductivity was determined from restivitiy and data was analyzed using Mott's polaron hopping models. Activation energy for conduction and density of states of carriers at Fermi level have been determined. It is confirmed that the charge transport in these systems is due to small polaron hopping at higher temperature and variable range hopping at lower temperatures.

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