

Direct Current Conductivity of Polyaniline-Cobalt Chloride Nanocomposite Prepared by Wet Chemical Route

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ABSTRACT

The direct current electrical transport properties of Polyaniline-Cobalt chloride nanocomposite is investigated in the present article. The X-ray diffraction pattern exhibits the presence cobalt chloride in the nanocomposite and also gives average size of the nanocomposite. Uniform morphology of the nanocomposite is obtained from Scanning Electron Microscopy. The dc transport property of the samples has been measured within a temperature range 77-300 K in presence and in absence of a transverse magnetic field up to 1Tesla. The dc conductivity has been explained in terms of the variable range hopping theory and the negative dc magnetoconductivity is found to follow the wave function shrinkage model.

Keywords: Nanocomposite, Polyaniline, Cobalt chloride, Charge transport, Magnetoconductivity.

1. Introduction:

During the last few decades, electrical properties of conducting polymers have been investigated extensively due to its potential application in electromagnetic interference shielding, molecular sensors, nonlinear optical device and microelectronic devices [1-5]. Among this class of materials, Polyaniline have relatively higher conductivity, better stability, cost effectiveness and can be easily synthesized [6-9]. Polyaniline gives semiconducting behavior with relatively high conductivity which can be enhanced by doping impurities due to delocalization of charge and spin along the polymeric backbone[10-16]. There are many investigations on doped polyaniline which gives an idea about its charge transport mechanisms . According to Kahol et al.[17-18]. quasi-one-dimensional (1D) variable range hopping (VRH) is the dominating charge transport mechanism for conduction in doped polyaniline while Sanjai et al.[19] found three dimensional (3D) VRH conduction in pure unblended polyaniline but 1D VRH for blended polyaniline. A transition from 3D VRH Mott to Efros-Shoklovskii at low

temperature has been shown by Ghosh et al.[16]. So there has been a controversy in the electrical properties of doped polyaniline samples. Only a detailed transport property study of this system can remove this confusion. Apart from the above studies several works describing the preparation of metallic ions or particles dispersed in polyaniline have been reported [20-22], but a very few has been reported with enhanced magnetoconductivity. The electronegative nitrogen of polyaniline attracts the positively charged metal ions by an electrostatic force in between different polymer chain layered structure [23]. Thus, to explore the effect of magnetic materials on the charge transfer mechanism of polyaniline, the electrical transport property of the polyaniline-cobalt chloride nanocomposites are measured in the temperature range $77 \leq T \leq 300\text{K}$.

2. Sample preparation and Characterization:

2.1 Materials: Aniline, Cobalt chloride, Hydrochloric acid, ammonium peroxydisulphate (APS), acetone, and ethanol were used as received from the market and purified them as required for this investigation. Aniline was double distilled under vacuum.

2.2 Synthesis of polyaniline: The typical synthetic process of Polyaniline-Cobalt chloride nanocomposite was performed as following: 1mmol aniline is mixed with 1 mmol Cobalt chloride (CoCl_2) solution so that aniline: CoCl_2 solution ratio becomes 1:10. Mixture is stirred slowly to prepare a homogeneous solution. 0.5 molar ammonium peroxydisulphate (APS) solution is prepared in 1molar HCL and kept it at 0°C for an hour. It is then added drop wise with continuous magnetic stirring and left the solution in refrigerator at rest for 24 hours to complete the polymerization process. It is then centrifuged at 10000 rpm for an hour. The solid mass obtain is washed with acetone, ethanol and double distilled water to remove monomer, oligomer and excess oxidant until the filtrate become colourless and dried in an oven at 40°C for overnight. We have prepared four samples using 0, 1, 2 and 5 milimolar Cobalt chloride (CoCl_2) solution for comparison purposes. Samples are marked as S_0, S_1, S_2, S_3 where S_0 is pure polyaniline and S_1, S_2, S_3 are Polyaniline-Cobalt chloride (CoCl_2) composites having 1, 2 and 5 milimolar Cobalt chloride (CoCl_2) solutions respectively.

2.3 Characterization: Morphology of these samples was measured by a scanning electron microscope (SEM, Hitachi S-3000N) on Au substrate. The phase identification of the fine powdered composite and polymer was performed using X 'Pert pro X-ray diffractometer with nickel filter $\text{Cu } k_\alpha$ radiation ($\lambda = 1.5414\text{\AA}$) in 2θ range from 20 to 80° . Fourier transform infrared spectrums (FTIR) were recorded with a FTIR-NEXUS, NICOLET instrument in the region of 500 to 2000 cm^{-1} using KBr pellet. To measure the temperature-dependent dc resistivity, standard four-probe method has been used with a Hewlett Packard 3458A Multimeter, Liquid nitrogen cryostat and an ITC 502S Oxford Temperature Controller. Fine copper wires have been used as the connecting wire and graphite paint as coating material.

3. Results and discussion

3.1 Morphology: Figure 1 shows the morphology of the polyaniline-cobalt chloride nanocomposite. From the SEM image it is observed that grains are well resolved, and circular in shape and from the Energy Dispersive Spectroscopy (EDX) analysis at different portion of the SEM image it is also confirmed that dopants were uniformly distributed in the polymer matrix. Uniform morphology obtained is due to no polymer chain entanglement during polymerization process [24].

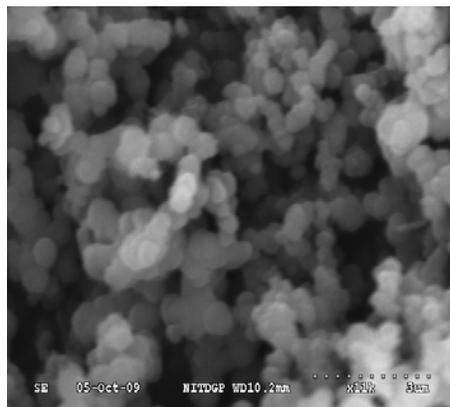


Figure 1: SEM image of Polyaniline-cobalt chloride nanocomposite (S_1).

3.2 Structural characterization: X-ray diffraction pattern (XRD) of pure polyaniline and Polyaniline-cobalt chloride composite is presented in figure 2. From the XRD pattern it is observed that pure polyaniline is amorphous but Polyaniline-cobalt chloride nanocomposite is crystalline. Polyaniline-cobalt chloride nanocomposite shows hexagonal rhombohedral crystalline structure (jcpds no 03-0869 respectively). Characteristic peaks observed are at $2\theta = 35.3, 51.19,$ and 63.72 for cobalt chloride doped polyaniline. So this XRD study confirms the presence of cobalt chloride in the polyaniline matrix. Average particle size (D) can be determined by the Scherrer formula: $D = k\lambda / \beta_{\text{eff}} \cos\theta$, where k is particle shape factor (generally taken as 0.9), λ is the wave length of $\text{Cu } k_{\alpha}$ radiation ($\lambda = 1.5414 \text{ \AA}$), θ is the diffraction angle of the most intense peak, and β_{eff} is defined as $\beta_{\text{eff}}^2 = \beta_m^2 - \beta_s^2$, where β_m and β_s are the experimental full width half maxima (FWHM) of the present sample and the FWHM of a standard silicon sample respectively. Grain size of our sample obtained using this formula is $\sim 30 \text{ nm}$.

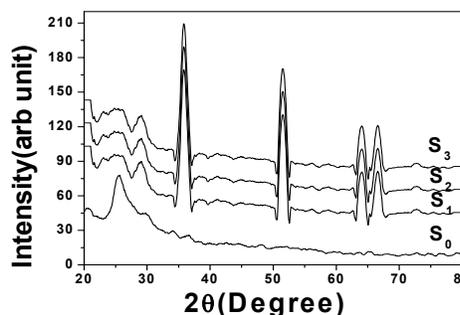


Figure 2: XRD of Polyaniline samples.

Fourier transform infra-red (FTIR) spectrum of pure polyaniline and polyaniline-cobalt chloride composite is presented in figure 3. Pure polyaniline has characteristic peaks at 1583.74, 1488.89, 1300.0, 1130, 818.74, 681.92 cm^{-1} . The band at 1583.74, 1488.89 cm^{-1} attributed to C=C and C=N stretching modes of vibration for the quinoid (-N=Q=N-where Q=Quinoid ring) and benzoid units, while band at 1300.0 cm^{-1} are assigned to the C-N stretching of mode of benzoid unit. The band at 1130 cm^{-1} is due to the quinoid unit of polyaniline. The band at 810 cm^{-1} is attributed to C-C and C-H stretching for benzoid unit of polyaniline and band at 681.92 cm^{-1} assigned to out of plane C-H vibration. The peak assignment revealed that the produced product was polyaniline. Incorporation of cobalt chloride in polyaniline matrix leads to small shift of the peaks and also decrease in the intensity of peaks, which indicates the structural change of polymer, occurs with doping. The band at 1583.74, 1488.89, 1300.0 cm^{-1} were shifted in doped polyaniline and it indicates the molecular interaction of dopant with different reaction site of polyaniline. This FTIR spectrum analysis also confirms the presence of cobalt chloride in the polyaniline matrix [25].

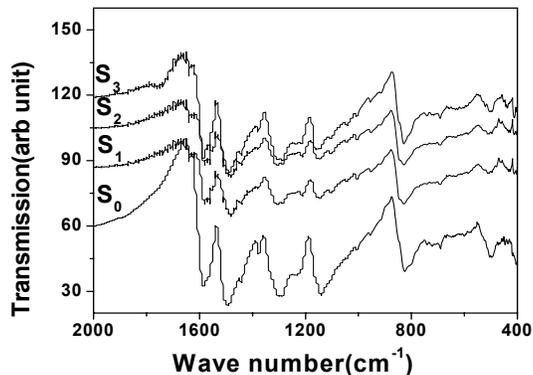


Figure3: FTIR of Pure polyaniline (S_0) Polyaniline-cobalt chloride nanocomposites (S_1 , S_2 and S_3).

3.2 Electronic transport property study:

The d.c resistivity of the of the Polyaniline-cobalt chloride nanocomposites are measured within a temperature range $77 \leq T \leq 300\text{K}$. The room temperature (300K) resistivities of the investigated samples are varying within a range $2.31 \times 10^3 \Omega\text{-m}$ and $2.94 \times 10^3 \Omega\text{-m}$ as listed in the table-1. The variation of conductivity with increasing concentration of Cobalt chloride in figure 4 reveals that introduction of the cobalt chloride in insulating polyaniline matrix significantly increases its conductivity. Figure 5 shows variation of the resistivity $\rho(T)$ with increasing temperature in absence of magnetic field. The resistivity of all the samples decreases with increasing temperature i.e, semiconducting behaviour is obtained for all the polyaniline-cobalt chloride nanocomposites. Generally, the temperature dependence of resistivity is explained by the Mott variable range hopping theory²⁶. According to this theory, resistivity can be expressed as

$$\rho(T) = \rho_0 \exp\left(\frac{T_{Mott}}{T}\right)^\gamma \quad (1)$$

where, ρ_0 is a constant, $T_{Mott} = \frac{24}{\pi k_B L_{loc}^3 N(E_F)}$ is the characteristics Mott temperature depending on the hopping barrier, electronic structure and energy distribution of the localized states, k_B is the Boltzmann constant, L_{loc} is the localization length and $N(E_F)$ is the density of states at the Fermi level. γ is the VRH exponent from which the dimensionality of the conducting medium can be determined by the relation $\gamma = \frac{1}{1+d}$. The possible γ values are 1/4, 1/3 and 1/2 for three, two and one dimensional system respectively. A linear variation is observed in the graph of $\ln\rho(T)$ with $T^{-1/4}$ in figure 5 throughout the entire temperature range indicating the three-dimensional hopping transport property. The values of T_{Mott} for all the samples have been calculated from the slope of the curves of figure 5 and are given in the table below. The value of T_{mott} in pure polyaniline is less than the nanocomposites. It may be due to the introduction of the cobalt chloride into the insulating matrix of polymer resulting in the localization of the electronic wave functions into the smaller regions.

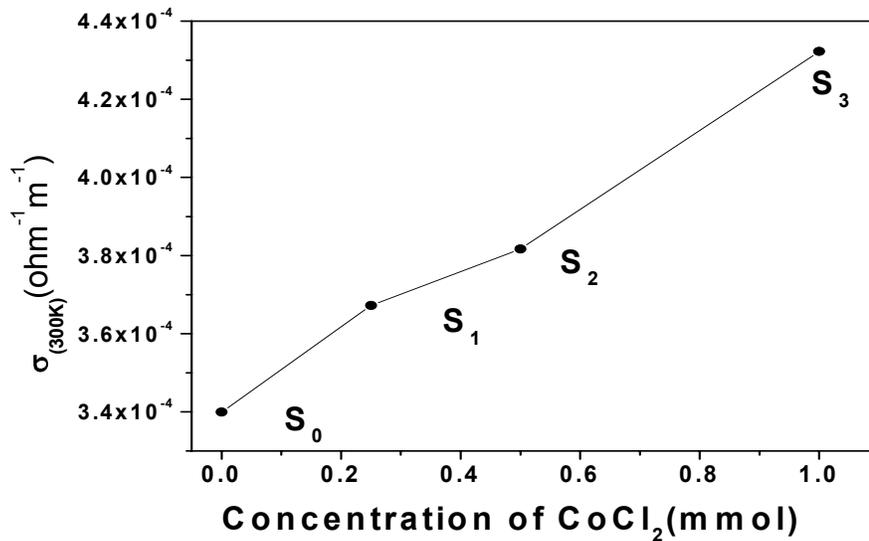


Figure 4: Variation of Conductivity at room temperature with concentration of cobalt chloride

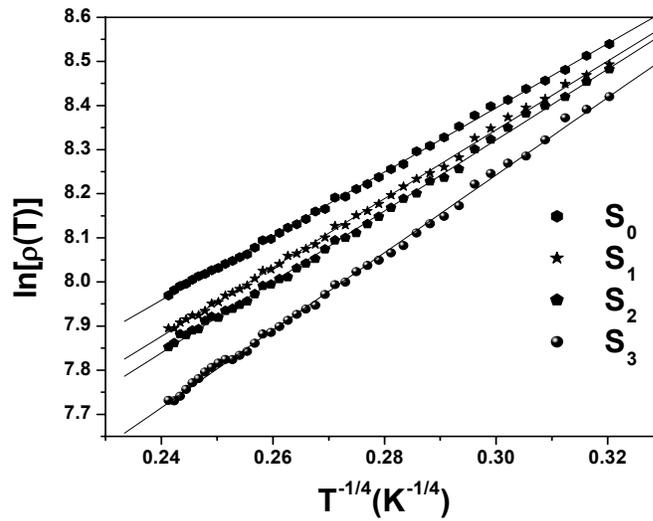


Figure 5: Variation of dc resistivity of S_0 , S_1 , S_2 and S_3 with temperature.

Table 1: Different physical parameters of Polyaniline-cobalt chloride nanocomposites:

Parameters	S_0	S_1	S_2	S_3
Concentration of $\text{CoCl}_2 \times$ (milimolar)	0.0	1	2	5
Resistivity at room temperature $\rho(300\text{K})$ ($\Omega\text{-m}$)	2941.41	2722.91	2619.91	2313.31
γ	0.25	0.25	0.25	0.25

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$T_{Mott}(K)$	2783.52	3705.70	4174.463	5961.296
$\rho_o (\Omega\text{-m})$	500.58	405.13	368.84	272.15
$L_{loc} (\text{Å})$	101.6	95.5	93.8	87.9
$N(E_F)$ (states/joule/2-rings)	1.89×10^{44}	1.71×10^{44}	1.6×10^{44}	1.36×10^{44}
$R_{hopp}(\text{Å})$	21.8	50.9	18.2	15.6

The magnetoconductivity of the Polyaniline-cobalt chloride nanocomposites has been measured under a transverse magnetic field up to 1 Tesla. All the investigated samples are showing negative magnetoconductivity at room temperature. The percentage change of conductivity $\left[\frac{\sigma(B,T) - \sigma(0,T)}{\sigma(0,T)} \times 100 \right]$ in

the presence of magnetic field 0.8T at 300K is about 0.02% whereas for the Polyaniline-cobalt chloride nanocomposites it is of the order of 0.21%. So there has been a noticeable increase in magnetoconductivity up on introduction of the cobalt chloride in the insulating polymer matrix. Direct current magnetoconductivity can be explained in terms of two simultaneously acting hopping processes, wave function shrinkage model²⁷⁻³¹ and the forward interference model (orbital magnetoresistivity)³²⁻³⁴. The forward interference model explains the positive magnetoconductivity. The effect of forward interference among random paths in the hopping process between two sites is spaced at a distance equal to the optimum hopping distance. On the other hand the wave function shrinkage model predicts that wave functions of the electrons reduce upon increasing magnetic field. As a consequence; average hopping length decreases resulting in negative magnetoconductivity. So the behavior of the investigated samples can be explained in terms of the wave function shrinkage model. Under a small magnetic field, the magnetoconductivity can be expressed as

$$\ln\left(\frac{\sigma(B,T)}{\sigma(0,T)}\right) = -t_1 \frac{e^2 L_{loc}^4}{\hbar^2} \left(\frac{T_{Mott}}{T}\right)^{3/4} B^2 \quad (2)$$

where, $t_1 = 5/2016$ and L_{loc} is the localization length. A linear variation of $\ln[\sigma(B)/\sigma(0)]$ with B^2 is shown in figure 6. The solid lines are the theoretical fit and the points indicate the experimental values. L_{loc} can be calculated from the slope of the straight line curve of figure 6. It varies between 8.79 nm to 10.16 nm for different samples. The average hopping length has been calculated by the formula $R_{hop} = (3/8)(T_{Mott}/T)^{1/4}L_{loc}$ which varies between 1.56nm to 5.09nm for different samples. The Values of ρ_0 is calculated from the slopes of Figure 5 and $N(E_F)$ is calculated from the known values of T_{Mott} and L_{loc} and is enlisted in the table. The localization length of S_3 is smaller in comparison with other samples. This is due to the presence of disorder. The extent of disorder present in the sample is generally expressed in terms of the resistivity ratio $[\rho(77K)/\rho(300K)]$. The resistivity ratio of S_0 is almost 8, whereas for other samples this value is restricted to 2.5. The higher value of resistivity ratio is S_0 indicates the presence of more disorder in pure polyaniline than nanocomposites.

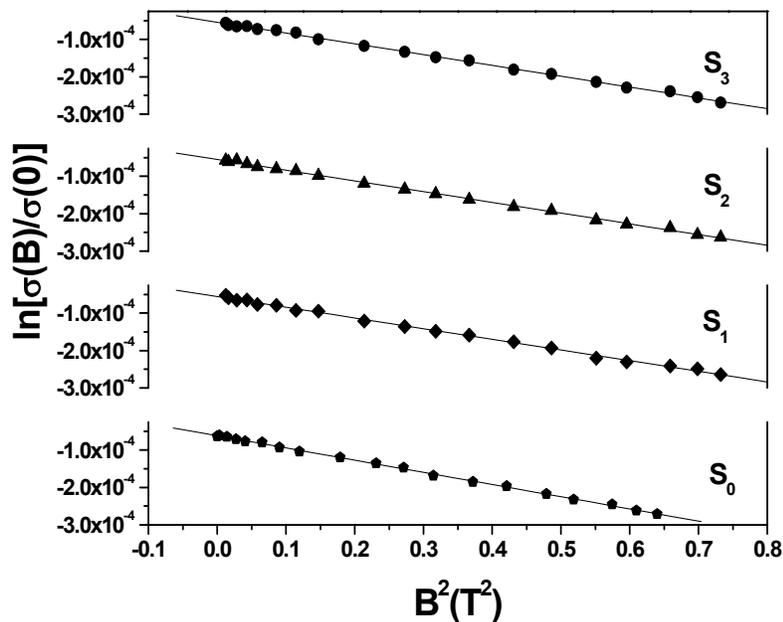


Figure 6: Variation of conductivity ratio of S_0 , S_1 , S_{2v} and S_3 with magnetic field.

4. Conclusion:

Polyaniline-cobalt chloride nanocomposites are prepared successfully by a simple wet chemical method. X-ray diffraction pattern gives the particle size as 30 nm. The SEM picture shows the uniform distribution of the cobalt chloride ($CoCl_2$) atoms in the Polyaniline matrix. The low temperature dc transport property of all the

samples follow the 3-D VRH model whereas the dc magnetoconductivity is found to follow the wave function shrinkage model.

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