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Synthesis, D.C. Electrical Conductivity and Activation Energy of Metal Sulphides Doped Polyaniline-Nanocomposite

Bhaiswar JB[1*], Meghe DP[1], Salunkhe MY[2] and Dongre SP[3]

[1]*Department of Physics, Nagpur Institute of Technology, Nagpur*
[2]*Department of Physics, Institute of Science, R.T.road, civil line, Nagpur*
[3]*Department of Physics, Bhalerao Science College, Saoner.*

***Corresponding author:** Bhaiswar JB, Department of Physics, Nagpur Institute of Technology, Nagpur, India, E-mail: jitendrabhaiswar@gmail.com*

ABSTRACT

The objective of the present investigation is to fabricate the CdS based polyaniline (PANI) nanocomposites which are prepared using chemical oxidation technique) with APS as oxidant by the simple polymerization reaction. Further, the chemical structure, morphological study and electrical properties such as FT-IR, XRD, and D.C electrical conductivity analysis are studied. The TEM is used to find the shape and composition of CdS nanoparticle. The electrical conductivity of CdS composite are determined using fore Probe methods. The Activation energy is calculated using the formula of different wt percentages' of cds nanocomposite and compare the result with bulk Polyaniline.

Keywords: Polymer, electrical conductivity, nanocomposite, activation energy.

INTRODUCTION

Nanotechnology is a supportive application in all fields of the research area in modern science. It possesses different shapes and sizes ranging from 1 nm to 100 nm [1]. Polymeric nanocomposites consisting of organic polymer and inorganic nanoparticles in a nanoscale regime represent a novel class of materials that have motivated considerable interest in recent years. These composites exhibit new advantageous properties and can be very different from those of their individual counterparts. It is therefore expected that this type of materials will play increasingly important roles in research and in numerous applications. They normally have particular properties and are important for many technological applications, ranging from microelectronics to catalysis, optoelectronic devices, and synthesis of lubricant and preparation of electrolytes for rechargeable batteries [1-4]. Polyaniline (PANI) is one of the most interesting conducting polymers due to its low cost, good processibility, environmental stability, unique active conduction mechanism [5] and reversible control of conductivity both by charge-transfer doping and protonation [6]. Inorganic semiconductors CdS, ZnS & PbS nanoparticles are the most promising materials used in various applications like sensors, optoelectronic devices and in solar cells. Studies on PANI-CdS nanocomposites have been reported by many researchers [7-10] and focused on electrical conductivity. This paper presents the synthesis and d.c. electrical conductivity of PANI-CdS and PANI-Pbs nanocomposites.

MATERIALS AND METHODS

All chemicals used in this investigation were of analytical reagent grade and used as received. Only aniline was distilled prior to use.

Synthesis of Polyaniline via chemical oxidative polymerization

Polymerization was dispensed by the chemical oxidization of aminoalkane within the presence of H2SO4 and APS (Ammonium per-sulphate) in 100 ml water each contend the role as dopant and oxidizing agent severally. (0.4 mol) APS was dissolved in 100 ml water during a four-neck spherical bottom reaction flask and zero.4 mol H2SO4 is additionally another underneath involuntary stirring for two hours. Aniline (0.4 mol) was stirred with zero.4 mol of H2SO4 in 100 ml water. The solution of APS in H2SO4 was then added drop-wise within the solution of aminoalkane with vigorous stirring on a magnetic stirrer for three hours to initiate the aminoalkane chemical process. The reaction was later dispensed at temperature for 6-7 hours with stirring. A dark inexperienced coloured PANI suspension was obtained with precipitation. The synthesized PANI washed with deionized water repeatedly till the liquid was fully colorless. Finally, the mixture was filtered by filtered assembly. A precipitate of polyaniline was dried at 60ºC to 800ºC in oven.

Characterizations

X-RD spectra of all samples were taken on Philips PW -3071, Automatic X-ray diffractometer using Cu-Kα radiation of wavelength 1.544 Å, continuous scan of 2ºC min., with an accuracy of 0.01 at 45 KV and 40 mA. Fourier Transform Infra-Red (FTIR) spectroscopy (Model: Perkin Elmer 100) of PAni: Cds nanocomposite was studied in the frequency range of 400 cm^{-1}-4000 cm^{-1}.

TGA thermograms of all samples were recorded on Perkin- Elmer Diamond TGA/DTA in argon atmosphere at a heating rate of 10°C/min. TGA profile were taken over the temperature range of 30°C-1000°C.The electrical conductivity measurement were made using four probe techniques.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of pure PAni in emeraldine base form, PAni/Cds Nanocomposite (25%) & cadmium sulphide powder. The XRD pattern of PAni shows the two broad peaks at 2θ=20 and 25 with (111) & (110) plane and has an amorphous nature [11]. The degree of crystallinity increased in Pani/Cds nanocomposite than pure Pani clearly indicated the uniform distribution of nanoparticles in the polymer matrix. The crystalline size of the crystalline particle can be determined using Debye Scherer formula [$0.9\lambda/_{\beta}$ Cosθ] and it is found that the grain size of PAni/Cds nanocomposite is (27.73 nm).

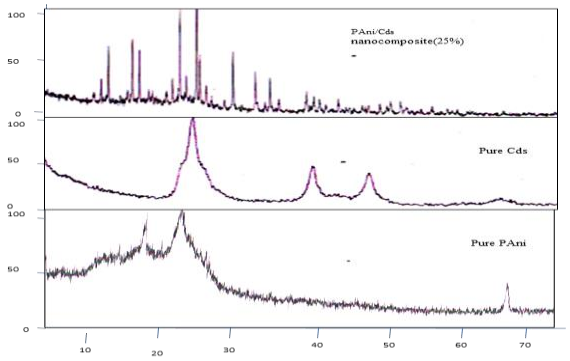

Figure 1: XRD pattern of PANI/CdS nanocomposite.

FT-IR Spectroscopy

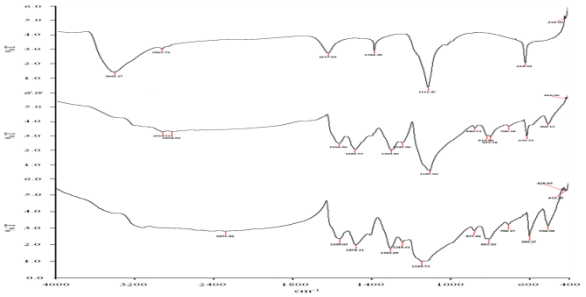

Figure 2: FTIR of PANI/Cds Nanocomposite.

Figure 2 shows the FT-IR spectra of pure PAni, Pani/Cds nanocomposite and pure Cds. The spectrum exhibit the clear presence of Benzoid at 1566 cm^{-1} Figure 2 shows the FT-IR spectra of CdS-polyanile nanocomposite was prepared under the optimal synthetic conditions. The presence of sharp peaks near 1478 and 1559 cm^{-1} are attributed to C=C stretching of the benzenoid and quinoid rings, respectively. The peak at 1240 cm^{-1} corresponds to C-N stretching of secondary amine in polymer main chain and can be clearly seen in the sample. The existence of absorption band at 1144 cm^{-1} has been interpreted as originating from plane bending vibration of C-H, which was formed in the structure of B–N+-M, Q-N+- M and N=Q=N during protonation of CdS to polyaniline. Absorption band near 2923 cm^{-1} is assigned to aliphatic C–H stretching of the polymer. A weak vibration absorption peak at 414 cm^{-1} for Cd-S bond was observed, shows the concentrations of CdS in the composites was low [12].

TEM of CdS-polyaniline NanoComposite

TEM images of synthesized Polyaniline nanostructures (PANI) shows a large quantity of interconnected branched Polyaniline nanofibers and capsule like structure. The pure Polyaniline are in the nanoscale range of 110 nm. The diameters of most fibers were found in the nanoscale 14 nm

range (Figure 3 & 4)

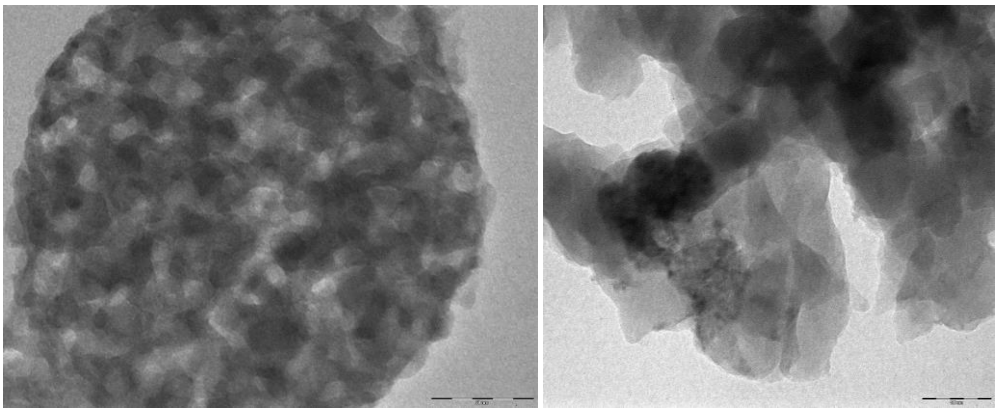

Figure 3: TEM Micrograph of Pure PANI and PANI/Nanocomposite.

D.C. Electrical Conductivity of Pure PANI & PANI/CdS Nanocomposte

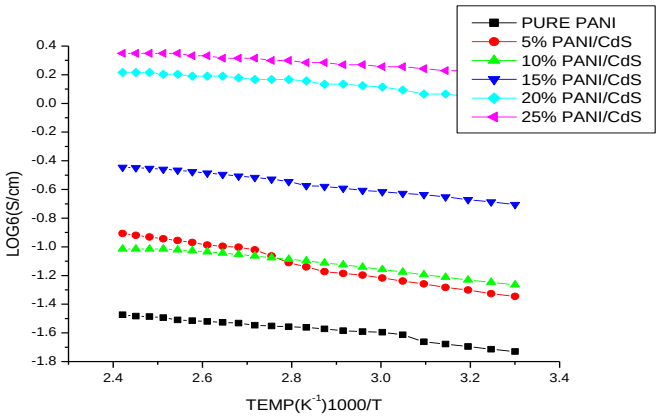

Figure 4: D.C electrical conductivity of PANi/Nanocomposite.

Table.1 shows the temperature dependence of DC-Electrical conductivity in the temperature range 303 K-413 K for undoped PANI and PANI/CdS nanocomposite. From the figure, it is evident that the DC-electrical conductivity of the nanocomposite is higher than that of pure Polyaniline. It is clear from the figure that all the samples, the plots of log (σ dc) vs. 1000/T are nearly straight lines, indicating that the conduction in these samples through an activated process having single activation energy in the temperature range 303 K-413 K. The activation behaviour of the samples are studied by using Arrhenius Equation.

$$\sigma = \sigma_0 e^{\frac{-E_a}{2kT}} \quad (1)$$

Where k is the Boltzmann's constant and σ0 is the conductivity at infinity temperature.

The values of activation energy calculated from Figure 4.1 and are given in Table 1. It was observed that D.C.electrical conductivity for PANI/CdS nanocomposite is higher than pure PANI. It is also observed that conductivity values is also increased with increased in weight % of CdS in PANI matrix. The value of conductivity for pure PANI and PANI/CdS nanocomposite and corresponding value of the activation is given in the Table 1. An increase in DC-conductivity with corresponding decrease in activation energy is found to be associated with a shift of Fermi level in doped samples [11]. From a single value of activation energy it is clear that the conduction is through the carrier concentration at the Fermi level. But the activation energy (Ea) alone does not provide any information whether the conduction takes place in extended states or by hopping in localized states. This can be explained on the basis of the values of pre-exponential factor (σo). A smaller value of activation energy is also indicating that a wide range of localized states and the conduction is taking place by the hopping process. From the above results we can conclude that the hopping mechanism is responsible for an increase in the conductivity of the samples. A smaller value of σ for PANI indicates that the density of defect states increases in the sample and further supports our argument that the conduction mostly takes place by the hopping process in the CdS doped Polyaniline. The formation of polarons and bipolarons can also be used to explain the conduction mechanism. Polarons and bipolarons play a leading role in determining the charge injection, optical and transport properties of conductive polymers. These are self-localized particles like defects associated with characteristic distortions of the polymer backbone and with quantum states deep in the energy gap due to strong lattice coupling.

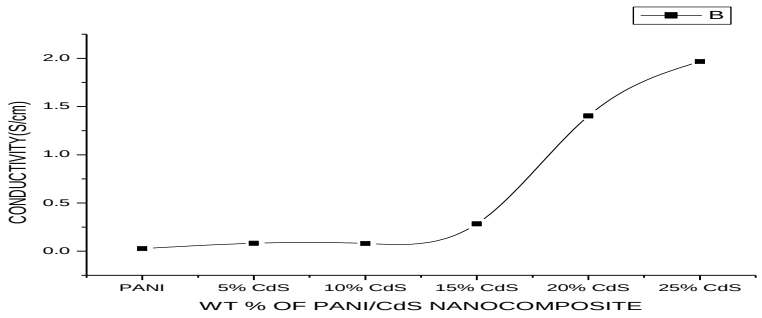

Figure 4.1: Variation Variation of electrical conductivity with Weight percentage of CdS

Table 1: D.c. conductivity and activation energy for pure PANI and PANI/CdS.

Sr.No.	**Material**	**Conductivity' σ (S/cm)**	**Activation energy, E_a(eV)**
1.	Pure PANI	$2.705X10^{-2}$	$3.97X10^{-4}$
2.	5% PANI/CdS	$8.22\ X10^{-2}$	$2.13X10^{-4}$
3.	10% PANI/CdS	$7.974\ X10^{-2}$	$1.2065X10^{-4}$
4.	15% PANI/CdS	$2.835\ X10^{-1}$	$1.226X10^{-4}$
5.	20% PANI/CdS	1.40224	$0.9191X10^{-4}$
6.	25% PANI/CdS	1.96766	$0.6786X10^{-4}$

CONCLUSIONS

In general, Polyaniline nanocomposites of different weight percentages of Cds were synthesized in a simple and eco-friendly route of chemical oxidation. The different CdS/PANI based composites were developed. The following FT-IR, XRD and TEM, also been done. Further, D.C.electrical conductivity and activation energy has also been studied. In general, PAni/CdS surface-treated nanocomposite properties were found to be excellent overall, compared to the untreated ones. Improved Electrical conductivity at different weight percentages of CdS was examined. The present investigation clear the Electrical conductivity could also be potential for industrial application when they are surface modified.

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