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Synthesis, Characterization and DC Conductivity Of PANI – CdO Composite

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Abstract: In the present paper we are reporting the synthesis, characterization, DC conductivity and activation energy of polyaniline (PANI) with cadmium oxide (CdO) composites at different weight percentage. PANI-CdO composites were synthesized by insitu chemical oxidation polymerization method using Ammonium peroxydisulfate (APS) as an oxidizing agent and are characterized using XRD, SEM and FTIR to investigate the structure and surface morphology of composites. The DC conductivity and activation energy are studied as a function of temperature in the range of 50 - 150^{0}C. The DC conductivity increased as temperature increases showing semiconducting nature of PANI and CdO composite.

Key words: DC electrical conductivity, polyaniline composite, SEM, XRD and FTIR, activation energy.

I. INTRODUCTION

Generally polymers have been considered to be good electrical insulators and their variety of applications are found in their insulating property only. But later, the discovery of electrical conduction in polyacetylene on exposure to halogens by genius Heeger, MacDiarmid and Shirakava, there opened a new field of electrically conducting polymers [1]. Nowadays conducting polymers are popular in the field of materials science due to their potential applications in many electronic devices [2-5]. Polyaniline is one of the most important conducting polymers, because of its solubility in some organic solvents leads to change in its electronic structure and physical properties by both charge transfer doping and protonation [6-9]. In general the change in properties makes polyaniline a versatile material. Polyaniline have the best combination of environmental stability, good conductivity and low cost. Particularly change in electrical properties of polyaniline with applications such as active electrode in batteries, in microelectronics, sensors, energy storage elements, organic light emitting diodes, as electro chronic material for displays, etc. In the present work the composites of polyaniline with CdO at different weight percentage were synthesized by chemical polymerization method using ammonium persulphate as an oxidizing agent. Cadmium oxide (CdO) is n-type semiconductor and has been used in application such as photo diodes, phototransistors, photovoltaic cells, transparent electrodes, liquid crystal displays, IR detectors etc. CdO microparticals undergo band gap excitation when exposed to UV light. With this background of multifunctionality CdO is used in composite preparation. The formation of PANI/CdO composites were characterized by XRD, SEM and FTIR.

2 EXPERIMENTAL MEASUREMENTS

SYNTHESIS OF SAMPLE

The chemicals of aniline monomer, Ammonium per sulfate (APS)$(NH_4)_2S_2O_8$, hydrochloric acid (HCl), and CdO were procured from Sd fine Chemicals Mumbai. The chemicals used were of analytical reagent (AR) grade. Aniline of 0.0548 mol was dissolved in 1M HCl to form aniline hydrochloride. CdO was added in different wt% to the above solution with vigorous stirring to keep CdO suspended in the solution. To this above reaction mixture the oxidant solution which was prepared by dissolving 0.022mol APS in 50 ml of distilled water, added drop wise with continuous stirring for about 2 hrs and the resulting mixture is kept overnight to polymerize completely. After one day the resulting precipitate is filtered and washed repeatedly with demonized water and finally the resultant precipitate was dried in an oven for 8hrs at 60 degree temperature. The dried powder of polyaniline with CdO composite is used to make a pellet by applying 5-6 tons of pressure using a pellet making machine [Model-UTM]. The silver paste is coated on both sides of surface of the pellet for providing electrical contacts.

3 RESULTS AND DISCUSSION

3.1 XRD of PANI and PANI-CdO Composite

The powder of polyaniline is used for XRD measurements using powder method of X-ray diffractometer [Model: Regaku]. The XRD spectrum of pure PANI is given in Fig1. It is noticed that a broad and diffused peak observed at an angle 2Ɵ = 26 degree. This shows polyaniline is amorphous in nature. The XRD spectrum for the composite of polyanilinewith CdO is given in Fig2. The peaks are occurred for the composite of polyaniline with CdO at an angle of 2Ɵ=38, 44, 65, and 77 which shows the composite has crystalline nature and there is modification in the structure of the composite.

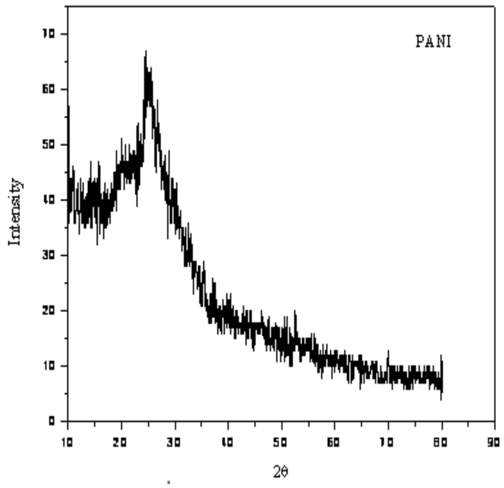

Fig1:XRD of pure PANI

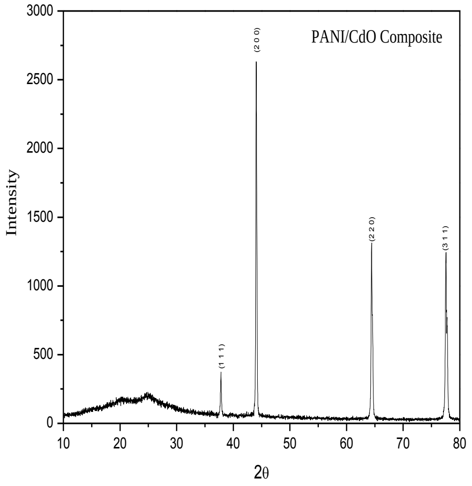

Fig2:XRD of PANI-CdO Compposite

3.2 SEM image of PANI and PANI-CdO Composite

The SEM image of PANI and PANI/CdO composite is shown in the Fig3 andFig4. It is confirmed from the images that particle size is in nanometer range. The size of particles in polyaniline is around 65nm and PANI/CdO composite is around 170nm.The SEM image also reveals that homogenous distribution of CdO in PANI.

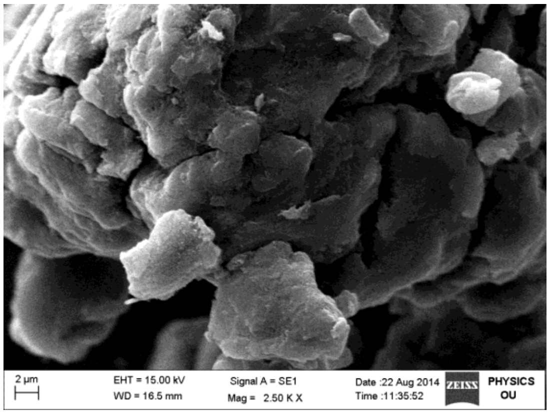

Fig3:SEM Image of PANI

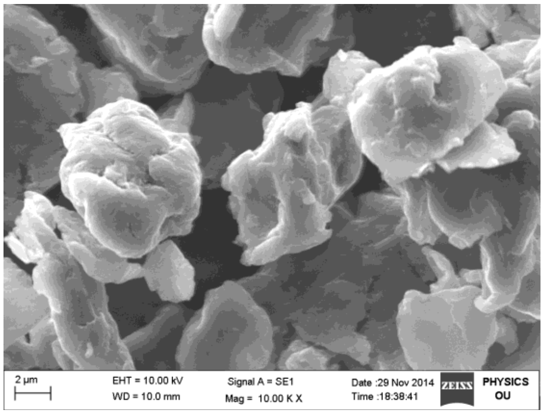

Fig4:SEM Image of PANI-CdO Composite

3.3FTIR Spectra of PANI and PANI-CdO Composite

The FTIR spectra of pure PANI are shown in Fig 5. The prominent absorption peak observed at 3466 cm^{-1} is due to N-H stretching mode of amines, 1471 and 1569 cm^{-1} are due to C=N and C=C stretching modes of vibration of an benzenoid and quinoid units of PANI, 2930 cm^{-1} is due to C-H stretching of alkanes, 1232 cm^{-1} is due to C-N stretching of benzenoid ring it is also a characteristic of conducting protonated form of polyaniline, 1295 cm^{-1} is due to N-O symmetric stretching of nitro compounds, 1147 cm^{-1} is due to vibration of C-H band in benzene ring, 935 cm^{-1} is due to C-H bending of aromatic ring, 582 cm^{-1} is due to metal oxygen stretching. Hence, the peak assignment reveals that produced polymer is an polyaniline. The FTIR spectra for PANI/CdO composite at 40 wt% are shown in Fig6. The composite have transmittance peaks at 712 & 586 cm^{-1} is due to metal oxygen vibration, 1124 cm^{-1} is due to C-N stretching of aliphatic amines, 1364 cm^{-1} is due to N-O symmetric stretching of nitro compounds, 1600 cm^{-1} is due to C-C stretching in aromatic rings, 1750 cm^{-1} is due to C=O stretching of aldihydes, 2840 cm^{-1} is due to C-H stretching of alkanes, 2930 and 3440 cm^{-1} is due to N-H bending. By comparing FTIR spectra of PANI and PANI/CdO composites it is observed, that in the composite, the characteristic stretching frequency is shifted towards higher wave number side which indicates the structural change of polymer due to addition of CdO particles.

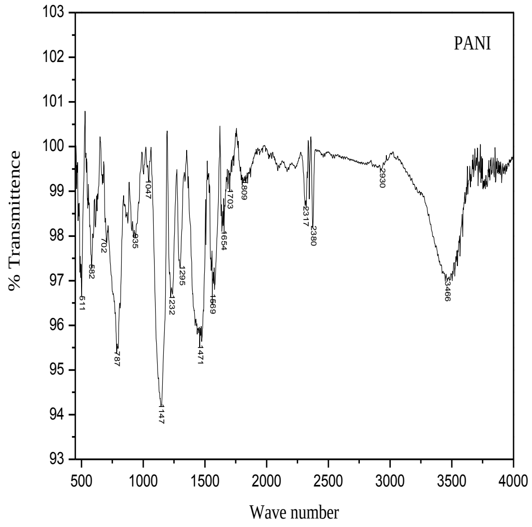

Fig5:FTIR Spectra of pure PANI

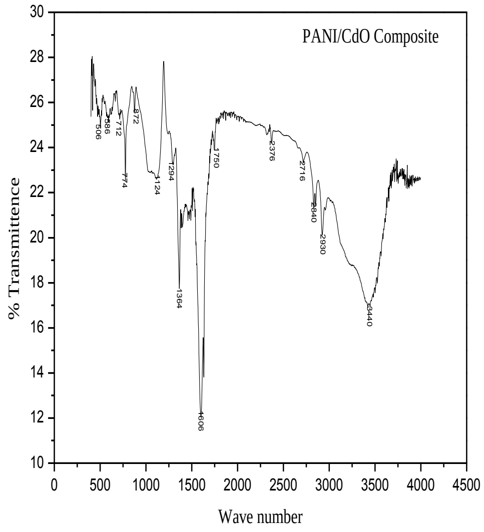

Fig6:FTIR Spectra of PANI-CdO Composite

3.3 DC Conductivity of PANI-CdO Composite

The DC conductivity is studied as function of temperature in the range of 50 – 150^{0}C for polymer of polyaniline and its composites PANI-CdO at different weight percentages. The DC conductivity for all the samples are obtained with the help of measured value of high resistance and dimensions of the sample using equation

$$\sigma_{dc} = \left(\frac{L}{RA}\right) Scm^{-1} \qquad (1)$$

Where L (cm) is the sample thickness, A (cm^2) is its area and R (ohm) is the resistance of the material.

It is noticed from the Figure7 that, among all composites of CdO in PANI, the value of DC conductivity is greater than PANI for 20, 30, 40 and 50 wt% of CdO in PANI but lesser for 10 wt% of CdO in PANI. The increase in conductivity for 20, 30, 40 and 50 wt% of CdO may be due to formation of more number of polarons in the widen band gap. Hence, for particular amount of CdO composition, the surface of PANI would be modified to have high conductivity and have much active surface. Such enhancement of DC conductivity values can be attributed to the uncoiling of polymeric chains due to strong interfacial interaction between CdO particles with PANI caused by their composition [10]. Decrease in conductivity at 10 wt% may be due to partial blocking of charge carrier hop occurs and as a result the conductivity decreases. The conductivity of polymers depends on the conjugation length and chain alignment of the polymer. This plays an important role in the transportation of charge carriers. There will also be a molecular reorganization upon heating, which renders the molecules in a favorable state for electron-hopping from one PANI Island to another. The analysis of temperature dependent of conductivity suggests that the charge transport mechanism in PANI as well as in all of its composites can be explained by the variable range hopping (VRH) of DC conductivity and is governed by the following relation,

$$\sigma_{dc}(T) = \sigma_0 \exp[-(T_0/T)^{\gamma}] \qquad (2)$$

Where σ_{dc} is the D C conductivity, T is the temperature and σ_0 is the conductivity at the characteristic temperature T_0. The exponent $\gamma = 1/(1+d)$ determines the dimensionality of the conducting medium. The possible values of γ are 1/4, 1/3 and 1/2 for three, two and one-dimensional systems respectively.

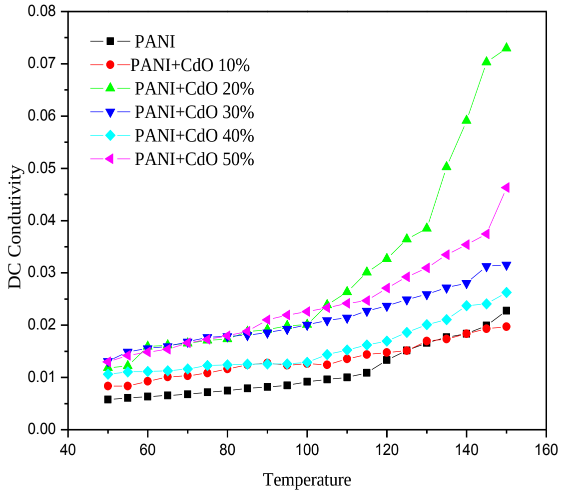

Fig7:DC Conductivity of PANI-CdO Composite

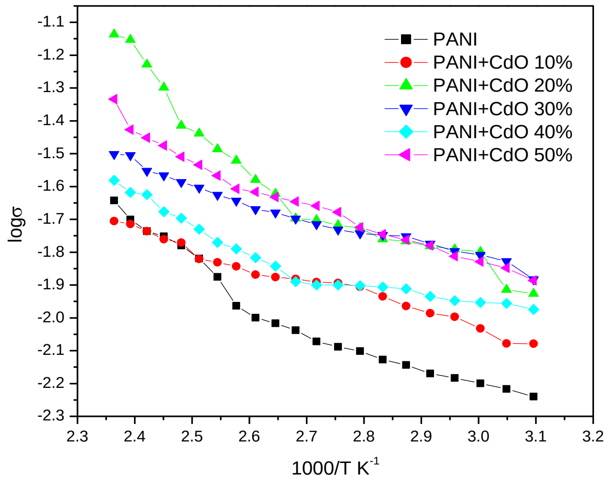

Fig 8:graph of log σ_{dc} vs 1000/T K^{-1} for PANI/CdO Composite

3.3 Activation Energy

The activation energy of polyaniline and its composite PANI-CdO, at different weight percentages have studied and analyzed in this section. Value of activation energy have been deduced using Arrhenius expression,

$$\sigma_{dc} = \sigma_0 \exp[-E_a/2k_BT]$$

$$\log(\sigma_{dc}) = \log(\sigma_0) - (E_a/2k_BT) \qquad (3)$$

Where σ_{dc} is D C conductivity, σ_0 is constant of a material, k_B is Boltzaman's constant (=1.38 x 10^{-23} Jk^{-1}), E_a is activation energy and T is absolute temperature. The activation energy E_a is calculated from the slope of the linear fitted line between log (σ_{dc}) vs 1000/T.

$$E_a = k \text{ x slope} \qquad (4)$$

Figure8 shows the graph of log (σ_{dc}) vs 1000/T, Arrehenius plots for polyaniline and its composite of PANI-CdO at 10, 20, 30, 40 and 50 weight percentages. The activation energy calculated and tabulated in the Table 1.

TABLE : 1

Weight percentage wt%	**Activation Energy E_a in eV For PANI-CdO Compoite**
10	0.1070
20	0.2169
30	0.0993
40	0.1142
50	0.1427

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4. CONCLUSION

The conducting polyaniline and its composite with CdO have been synthesized successfully using chemical oxidation method. The XRD spectrum for PANI-CdO composite is crystalline in nature. The peak positions are also differs from the pure CdO and this indicates the modification in the structure of the composite. From the SEM it can be confirmed that particle size is in nanometer range, also reveals that homogenous distribution of CdO in polyaniline. The FTIR spectra shows characteristic transmittance peeks at 1471 and 1569 cm-^{1} which are due to stretching of benzenoide and quenoide units of PANI which confirms the formation of PANI. It is observed from the transmittance spectra of composites, there is a homogeneous mixing of CdO in PANI and formation of new composite. The characteristic peeks are shifted towards the higher wave number side this may be attributed due to the Vander Waals interaction between polymeric chain and the oxides. The DC conductivity increased as temperature increases showing semiconducting nature of PANI and its composites, this may be due to thermally activated behavior of the conducting polymer.

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