

Studies on Synthesis and Electrical Properties of CdS-Polyaniline Nanocomposite via Oxidation Polymerization

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Abstract Nanocomposites of conducting polyaniline with CdS nanoparticles have been synthesized via in situ by oxidizing the complex of aniline with cadmium sulfate at 3.5 pH. The effect of CdS-nanoparticles on the electrical conductivity of polyaniline was discussed. The as prepared products were characterized by FT-IR and Transmission electron Microscopy. FTIR absorption band at 3600 - 3500 cm^{-1} confirmed the highly attached polyaniline with CdS nanoparticles. TEM showed the CdS particles are spherical with the average diameter of 19 nm which was evenly distributed in polymer matrix. The uniform intercalation of CdS nanoparticles results in a cooperative phenomenon between the polyaniline and the nanoparticles, as a consequence, the CdS nanoparticles increased the electrical conductivity of polyaniline nanocomposite to 6.50×10^{-2} S/cm compared to the pure polyaniline (10^{-10} S/cm); Germanium (10^{-2} S/cm) and Silicon (10^{-4} S/cm) semiconductors. Its electrical conductivity was found to be analogous with existing semiconducting metals. The fact is supported by the ample of experimental results and characterization evidences.

Keywords Nanocomposites, Nanoparticles, Cadmium Sulfide, Polyaniline, Electrical Properties

1. Introduction

The nanocomposites of metal and semiconductor particles are important in several optical and electronic applications[1] and their preparation with significant effort on the ability to control the size and morphology via innovative synthetic approach is highly challenging particularly by using organometallic precursors. Intrinsically, conducting polymers like polyaniline have potential for wide variety of application in electronics, sensors, LED, etc owing to its easy polymerization and environmental stability[2–5]. Properties of polyaniline can be tailored by changing its oxidation states[6], acid dopants[7, 8] or through blending it with other organic or inorganic nano sized semiconducting particles[9]. It has been described that the large internal interface area in nanocomposites enables an efficient separation of charge, which is important for photovoltaic applications[10]. Polyaniline-CdS nanocomposite has been already used in photovoltaic application but formation of ionic by-products (in the reaction during the synthesis that influences the electrical properties of resulting material), indicated some restrictions in preparation of nanocomposites. There are

several reports describing nanocomposites of polyaniline with semiconducting particles such as TiO_2 , PbS and CdS [11]. Polyaniline can exist in various oxidation states[12] exhibiting different properties. Transport properties of polyaniline transition metal salt composite have been studied[13]. Emeraldine base (EB) of polyaniline has been commonly used, as it is the most stable form of polyaniline. Enzymatic and gas-phase plasma have been utilized in the synthesis of polyaniline[14-17]. Unfortunately, options for the processing of polyaniline are limited, since this polymer decomposes prior to melting and it is only soluble in a few organic solvents, e.g. strong acids. This situation severely restricts the synthetic routes and desires challenging methodology for the preparation of polyaniline nanocomposites. To overcome this restriction, attempts are desired to synthesize the CdS-polyaniline nanocomposite through oxidative polymerization using hydrogen sulfide gas in solution. This study revealed a successful synthesis of incorporation of CdS-nanoparticles into polyaniline by simplest route and reported conductivities and dielectric property of CdS-polyaniline nanocomposite.

2. Experimental

2.1 Reagents and Materials

All chemicals used were of AR grade, Aniline was dis-

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tilled twice prior to use. Cadmium sulfate ($\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$), ammonium peroxydisulfate [$(\text{NH}_4)_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$], hydrochloric acid, ethanol were analytical reagents and were used as received.

2.2 Synthesis of CdS-Polyaniline Nano Composite

Polyaniline emeraldine base (EB) and its hydrochloric salt (Polyaniline-HCl) were prepared according to the procedure reported in literature [18]. CdS-polyaniline nanocomposite was synthesized as follows:

Quantitative amount of 0.1 M $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ was added into the 100 ml 0.5 M aniline solution. The solution was stirred continuously for two hours to get complete dissolution under inert atmosphere of nitrogen gas. 0.5 M $(\text{NH}_4)_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ solution was added drop wise with bubbling of H_2S gas at 3.5 pH. The reaction was carried out with constant stirring for 24 h at room temperature. The products were washed thoroughly plenty of times with 95 % ethanol and acetone. The resulting product was dried in oven at 60°C for 24 hrs. The product was named as CdS-polyaniline nano composite.

2.3. Characterization of Samples

The nanoparticles formed were characterized by JEOL 2010F transmission electron microscopy (TEM). The FT-IR spectroscopy (Perkin-Elmer 100 FT-IR spectrophotometer) was used to record spectra using KBr pellets. The electrical conductivity of the samples was measured at temperature range from 30°C – 100°C with dry pressed pallets using DFP-02 four probe set up. The capacitance and D-factor of thin pallet of a polymer sample were measured as a function of temperature using Direct Reading, LCR bridge, 8 C (Pacific), at frequency 1 KHz.

3. Result and Discussion

3.1. FT-IR of CdS-Polyaniline Nano Composite

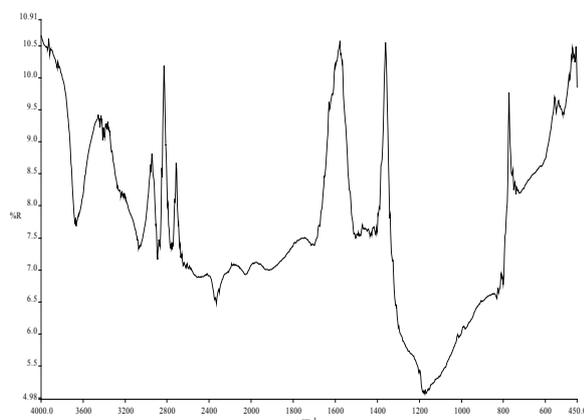


Figure 1. FTIR Spectra of CdS-polyaniline nanocomposite

Fig. 1 shows the FT-IR spectra of CdS-polyaniline nanocomposite was prepared under the optimal synthetic conditions. The presence of sharp peaks near 1510 and 1605 cm^{-1}

are attributed to C=C stretching of the benzenoid and quinoid rings, respectively. The peak at 1298 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 1120 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. The broad absorption band ranges from 3600 to 3500 cm^{-1} was attributed to the protonation of amines functional group at polymer backbone and was observed for the highly attached polyaniline with CdS. Absorption band near 2900 cm^{-1} is assigned to aliphatic C–H stretching of the polymer. A weak vibration absorption peak at 405 cm^{-1} for Cd–S bond was observed, shows the concentrations of CdS in the composites was low.

3.2. TEM of CdS-polyaniline Nano Composite

For the TEM characterization, a drop of the sample was placed on a carbon film supported by a copper grid in order to obtain electron micrographs in a JEOL 2010F Electron Microscope.

Fig. 2 shows a micrograph of CdS nanoparticles. The shape of the particles is spherical and the average diameter is 19 nm which was evenly distributed in polymer matrix. The high resolution micrographs of these nanoparticles display a crystal array as shown in Fig. 3



Figure 2. TEM image of CdS nanoparticles

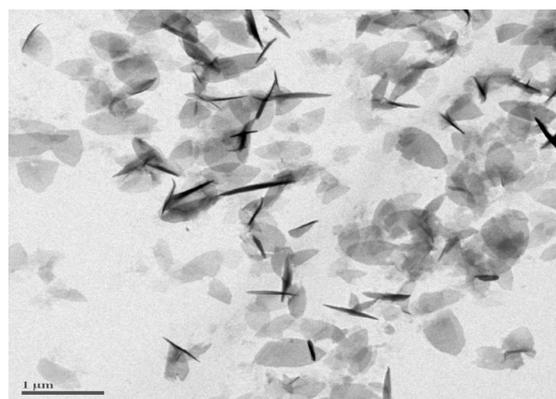


Figure 3. TEM image of CdS-Polyaniline nanocomposite

3.3. Electrical Conductivity

The temperature dependence of the electrical conductivity data (in the middle range of temperature) fit the Arrhenius type of equation (1) in the temperature range investigated,

$$\sigma(T) = \sigma_0 \exp(-E_0/2kT) \quad (1)$$

It was observed that CdS-Polyaniline nanocomposite exhibited high conductivity than pure polyaniline reported in table 1.

Table 1. Observed conductivities of CdS-polyaniline nanocomposite

Nanocomposite	Conductivity (S cm ⁻¹)
CdS - Polyaniline	6.50x10 ⁻²

The activation energy $\sigma_0(T)$ was calculated from Arrhenius equation presented in table 2.

Table 2. Conductivity, Activation energy, and Dielectric constant of CdS-polyaniline nanocomposite

Name of composite	$\sigma(T)$ cm ⁻¹ ohm ⁻¹	Activation energy (eV)	Dielectric constant (ϵ')
CdS-Polyaniline	6.50x10 ⁻²	0.30	1.15 x 10 ²

The temperature dependence of electrical conductivity of CdS-polyaniline nanocomposite shown in figure 4.

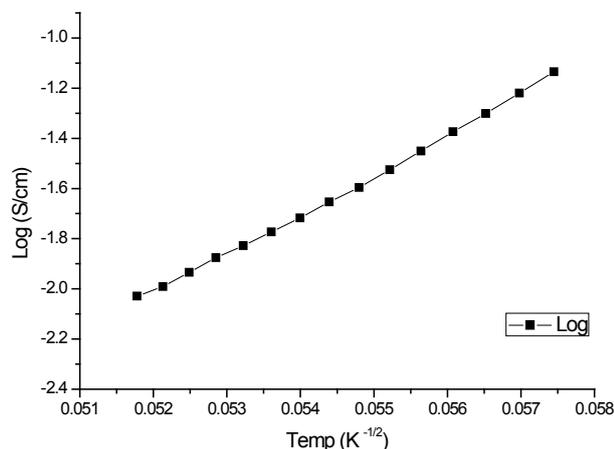


Figure 4. Temperature dependence of electrical conductivity of CdS-polyaniline nanocomposite

FTIR spectra demonstrated that CdS nanoparticles had been successfully incorporated into polymer chain. From this result it is believed that intercalation of CdS nanoparticles in polyaniline were helped to increase the conductivity due to enhancement of crystallinity of CdS nanoparticles. The conductivity of CdS-polyaniline (6.50x10⁻² S/cm) nanocomposite was greater than pure polyaniline (10⁻¹⁰ S/cm)[19], Germanium (10⁻²S/cm) and Silicon(10⁻⁴S/cm) semiconductors.

Thus in the present work ,cadmium sulfate and hydrogen sulfide gas was found to be more suitable for insitu preparation of CdS-nanoparticles in polyaniline matrix. The reaction of cadmium sulfate–polyaniline solution with H₂S gas resulted in formation of nano-sized CdS (without leaving any stable by-product) at room temperature. No other gas like

methane[20] was formed as a by-product in this reaction.

4. Conclusions

Polyaniline-CdS nanocomposites have been successfully synthesized via in situ by oxidation polymerization. FT-IR spectra demonstrated that the transition metal salt had been incorporated into polymer chain. Electrical conductivity of polyaniline–CdS nanocomposites was found to be increased when compared to pure aniline due to its increase in crystallinity. Electrical conductivity of CdS-polyaniline nanocomposite was found to be analogous with existing semi-conducting metals. Cadmium sulfate in aqueous medium has been used for the first time with polyaniline and also it is the first attempt to produce nanocomposite of polyaniline-CdS via in-situ with oxidation polymerization by simplest route.

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