Effect of Cobalt Sulphate Doping on Optical and Structural Properties of Poly [(Thiophene-2, 5-diyl)-co-para-methyl benzylidene]

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Abstract

Cobalt doped and undoped polymer composites of Poly [(Thiophene-2, 5-diyl)-co-para methyl benzylidene] were synthesized using catalyst phosphorous oxychloride by polycondensation method in a one pot at normal laboratory condition. The effect of cobalt doping on optical and structural properties of polymer composite have been evaluated by using UV-visible spectroscopy, x-ray diffraction(XRD), Field emission scanning electron microscope (FE-SEM), BET surface area measurement and thermal stability. Due to cobalt doping optical band gap of polymer composite slightly increased from 2.54 to 2.68 eV. The average crystallite size decreased slightly from 58.10 nm to 56.84 nm for undoped and doped samples respectively, as calculated by using well known Scherrer's formula. FE-SEM confirmed the interconnected porous morphology. Thermogravimetric analysis of both the polymer composites showed thermal stability up to 150 ^{o}C. BET analysis confirmed that surface area increased from14900 to 33900 cm^2/g. extremely due to doping. Hence can be useful as semiconducting material as well as plenty of applications where high surface area is required.

Keywords: Polymer composite, cobalt doping, surface area, thermal stability.

INTRODUCTION

Conjugated polymers are useful in both fundamental and practical studies as they have electrical and electrochemical properties parallel to both semiconductors and metals. Therefore they are as called conducting polymers. There are many reviews discussing the fundamental and technical features of conducting polymer nanocomposites materials [1, 2]. There are number of methods have been applied to put inorganic nanoparticles into the host-conducting polymer matrix which mainly involve electrochemical and chemical methods. The insertion is usually through ex-situ where the inorganic nanoparticles are prepared separately and then added to the conducting polymer matrix in different compositions during the polymerization reaction. Similarly, in situ polymerization techniques have also been used to synthesize inorganic-in-organic nanocomposites in which the inorganic nano particle is inserted in the conducting polymer matrix at once during polymerization in the same reaction vessel [3, 4].The insertion of metal in conjugated polymer has attracted attention during the past several years due to exceptional physical properties and wide application potential in diverse areas [5]. The capability to finely disperse the secondary species in the polymer confirms high surface area and possible improvement of the exclusive features of the composite [6, 7]. In 2003 Athawale and his co-workers have manufactured a Cu/PANI complex which has been used as a catalyst for the conversion of alkenes to ketenes or aldehydes in a single step [8]. Graphene/PANI composites have been synthesized by mixing [9] in situ polymerization [10] and electro-polymerization [11]. Though, when the complex is mixed with binders or additives to produce electrodes, its structure and electrical conductivity are significantly affected [12]. Identified these several findings, the preparation of new nano complexes with metal nanoparticles of countless significance [13,14] as these new materials have remarkable characteristics and features that may offer themselves to nano-technology applications. Porous polymer composites have wider

applications in catalysis [15]. Insertion of metallic nanoparticles into conducting polymer improved thermal stability, optical and structural properties [26].Conjugated polymers synthesized from copolymerization of different monomers in situ chemical polymerization having small density and high specific surface area which are useful where large surface area is required [17].

EXPERIMENTAL DETAILS

One pot synthesis of Poly [(thiophene-2, 5-diyl)-co-para-methyl benzylidene] polymer composite in the powder form can be achieved by chemical oxidative polycondensation method without need to any special equipment. Polycondensation between p-methyl benzaldehyde and thiophene was carried out to obtained methine type conjugated polymer.

Materials:

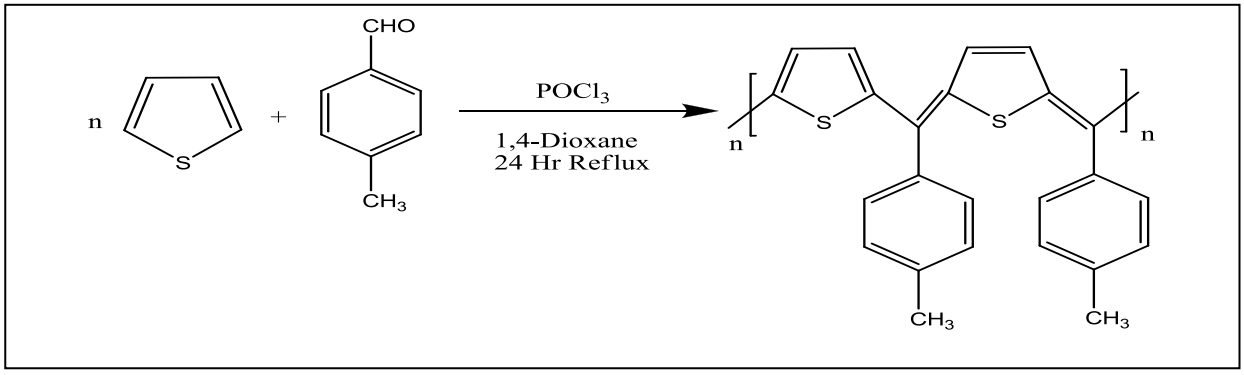
All the chemicals like Thiophene, 1, 4 dioxan and p-methyl benzaldehyde, Phosphorous oxychloride, methanol and Cobalt sulphate were purchased from Sigma-Aldrich, India, and were used without further purification.

Synthesis of Poly [(thiophene-2, 5-diyl)-co-para-methyl benzylidene]

Conducting conjugated polymer Poly [(thiophene-2, 5-diyl)-co-p-methyl benzylidene] synthesized by oxidative polymerization from thiophene and para methyl benzaldehyde in one pot at normal laboratory conditions. Thiophene (0.002 mmoles) and p-methyl benzaldehyde (0.002 mmoles) were refluxed electrically in paraffin oil bath at 87^{o}C for 24 hours in 15 ml neutral solvent 1, 4 dioxan and in presence of catalyst (0.002 mmoles) $POCl_3$ which also act as dehydrating agent. The reaction was monitored by TLC. After the completion of reaction 100 ml methanol is added to obtain the product. Then fine dark brown powder obtained by filtration was purified using methanol and finally dried at room temperature for 24 hours. The **scheme 1** shows the formation of Methine Bridge conjugated polymer.

Synthesis of doped Poly [(thiophene-2, 5-diyl)-co-para-methyl benzylidene]

Synthesis of doped polymer composite was carried out by the similar method as mentioned above. After 22 hours 0.1 gram cobalt sulphate dopant is added in the reaction vessel under the similar conditions. The final product obtained as mentioned previously and purified using methanol and used as synthesized for further characterization.



Instrumentation:

The UV-Visible spectrum of sample was taken using UV- visible SHIMADZU 2450 instrument in dichloromethane (CH_2Cl_2) in the range of wavelength 300-1000 nm to investigate conjugation. The UV-Vis spectroscopy is also used to know the optical properties of the material as well as for estimation of optical band gap. X-ray diffraction (XRD) measurements were carried out by using Bruker D8 Advance diffractometer having CuKα incident beam with λ = 1.5406 Å in 2θ range from 20 to 80 degrees. Field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, and 15 kV) coupled with an energy-dispersive X-ray spectrometer (EDAX) was used to analyze the

surface morphologies and chemical composition of samples. Surface area was measured by Brunauer-Emmett-Teller (BET) method by using (ASAP-2010 Micrometrics).Thermogravimetric analysis was carried out using thermal analyzer (TGA 50) under the stream of nitrogen gas (flow rate 50ml/min) was monitored around the sample chamber to minimize heat dissipation during measurements. The weight loss is plotted as function of temperature to get thermogram.

RESULTS AND DISCUSSIONS

Optical absorption studies

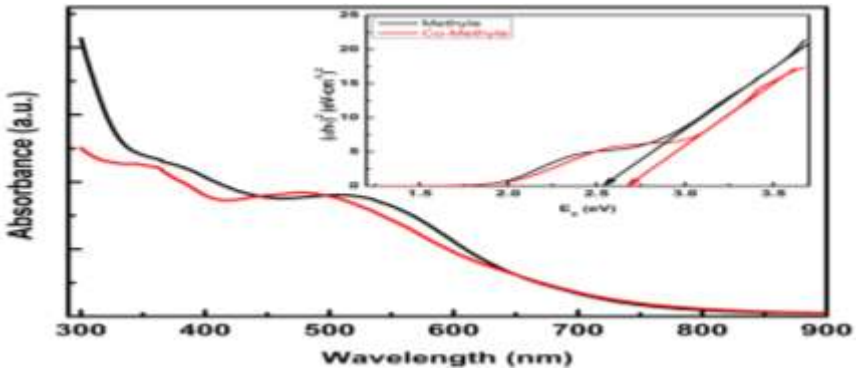


Figure1 Optical absorption spectra of the synthesized undoped and cobalt doped Poly [(Thiophene-2, 5-diyl)-co-p-methyl benzylidene] in dichloromethane as a function of wavelength. Inset shows corresponding plots of $(\alpha h\nu)^2$ vs photon energy (hν) for respective polymer solutions.

Figure 1 shows the variation in optical absorbance of polymer solution in dichloromethane after and before doping of cobalt as a function of wavelength. After doping of cobalt, the optical absorption spectrum of polymer shows slightly lower absorption than undoped polymer. It is also observed that for doped polymer solution the absorption edge is shifted towards lower wavelength which confirms increase in optical band gap value for doped sample. UV-Vis absorption spectra showed strong absorption bands at around 477 nm and 512 nm for doped and undoped samples, respectively.

In present study, undoped and Cobalt doped methyl polymers are having direct band gap with the exponent n=1/2 and is measured by plotting $(\alpha h\upsilon)^2$ versus hυ. The extrapolation of the straight line in the graph to $(\alpha h\upsilon)^2 = 0$ gives the value of the energy band gap (inset). The values of optical band gap was obtained are 2.54 eV and 2.68 eV for undoped and cobalt doped polymer materials, respectively. The neutral conjugated polymers are usually semiconductors.

Structural studies:

The structural properties of Methyl undoped and doped material were studied using X-ray diffraction (XRD) patterns. Figure 2 shows the XRD pattern of powder sample for (a) undoped and (b) doped material. The synthesized material showed intense XRD peak indicating crystalline nature of the undoped and doped samples. In the prepared sample the value of crystallinity is about 55.3% and 54.4% for undoped and doped samples, respectively which indicate that the crystallinity slightly decrease by doping of cobalt in polymer. The average crystallite size was found to be around 58.10 nm and 56.84 nm for undoped and doped samples, respectively as calculated by using well known Scherrer's formula.

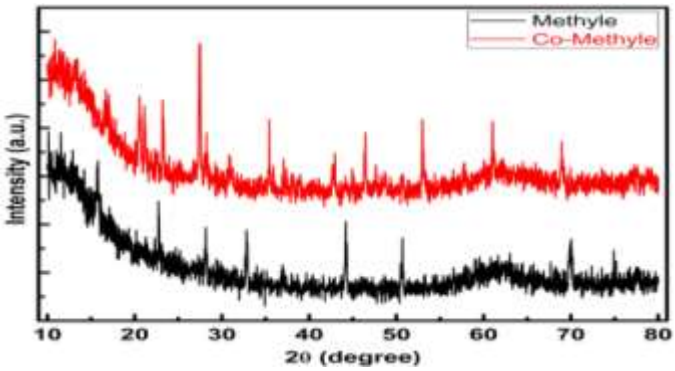


Figure 2 XRD patterns of Poly [(thiophene-2, 5-diyl)-co-p-methyl benzylidene] powder sample (a) undoped and (b) doped.

Surface morphological studies EDAX and BET measurement

Figure 3 shows the morphological characterization by using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, and 15 kV) unit. The FE-SEM images of powder sample of polymer were taken on the carbon tap mounted on sample holder. Figure (a) and (b) shows the surface morphology at lower magnification for undoped and doped samples, respectively. Inset shows FE-SEM images at higher magnification for respective samples. Figure (c) and (d) EDAX pattern of undoped and doped polymer samples. Whereas the inset of figure (c) and (d) shows the tabulated form of elemental composition of the respective sample. The elemental analysis confirms the presence of C and S peaks. The inclusion of Cobalt in addition of C and S in the doped sample confirms the doping effect. The size and dimensionality of this kind of structure can be tunable by altering the synthesis conditions. FE-SEM image shows the uniform formation of material and interconnected with each other with porous structure leading to high surface area which is beneficial for plenty of applications. BET technique was used to know the porosity and measure the value of actual surface area. Before analysis, all the samples were degassed at 70 ^{o}C with 10^{-5} Torr for 1 hour. Surface area is being measured by the quantity of absorbed and deabsorbed gas from the surface of the sample with respect to the change in the thermal conductivity of the mixture of nitrogen and helium gas. The obtained surface area of undoped and doped samples is 14900cm^2/g and 33900cm^2/g, respectively. Increase in the surface area of the adsorbent, increases the total amount of gas adsorbed. The BET analysis is in correlation with FE-SEM results.

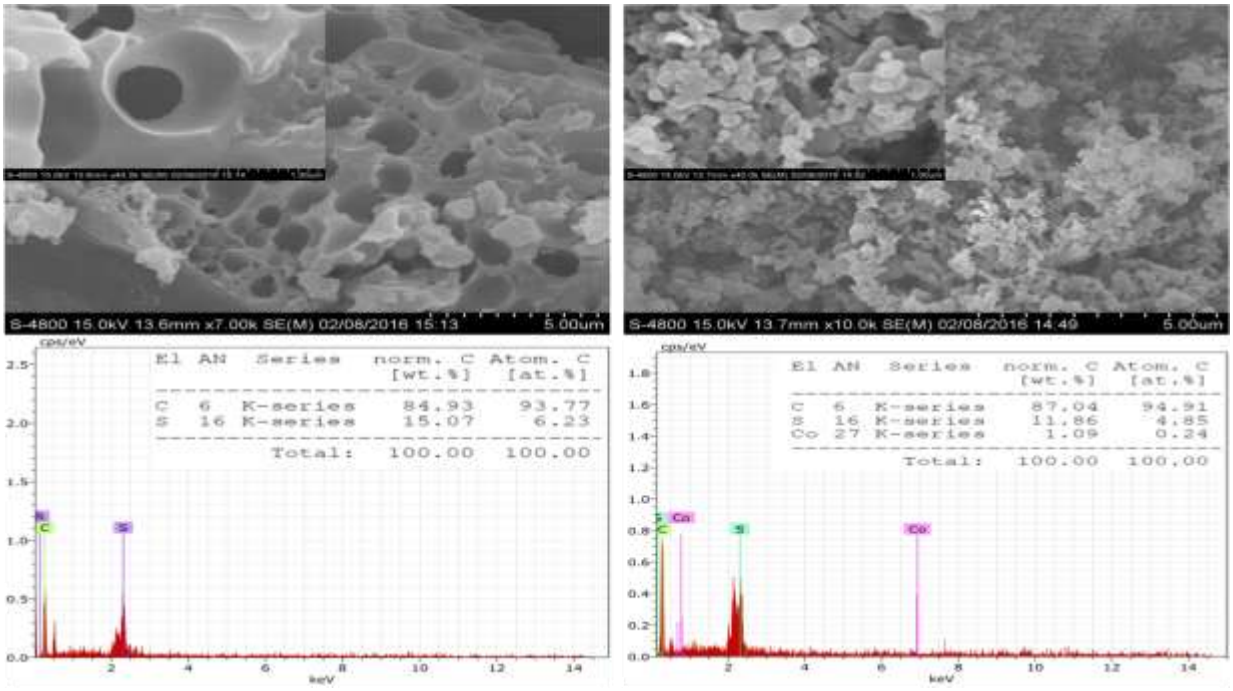


Figure 3 Surface Morphology and EDX of Poly [(thiophene-2, 5-diyl)-co-p-Methyl Benzylidene] powder samples (a) and (c) undoped and (b) and (d) doped.

Thermal Stability

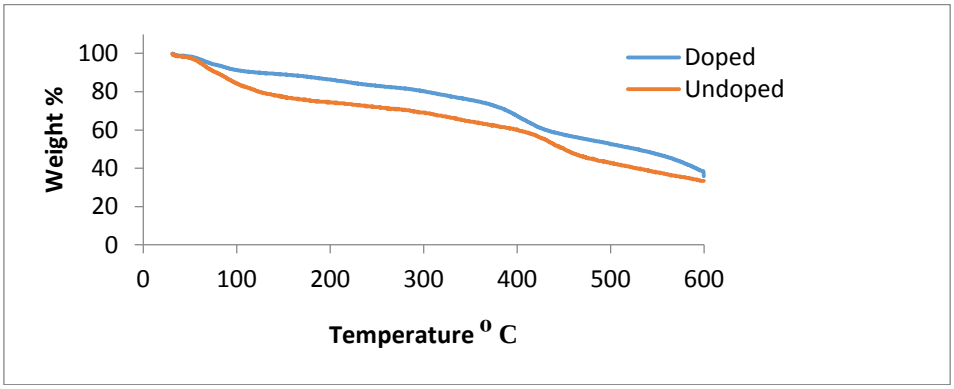


Figure 4 TGA of Poly [(Thiophene-2, 5-diyl)-co-para-methyl benzylidene]

Undoped and doped polymer matrices are thermally stable with negligible weight loss during 70°C to 110°C temperature. The first step is predictable to the loss of water molecules trapped in the polymer matrix 10 % for doped and 27 % for undoped. Above100°C there is negligible weight loss up to 400°C for cobalt doped and undoped samples due to the elimination of counter ions. It was observed that doped Poly [(Thiophene-2, 5-Diyl)-co-para-methyl benzylidene] is slightly more thermally stable up to 150°Cthan undoped. There is significant drop in both samples around 400°C due to decomposition of the carbon skeleton.

CONCLUSIONS

In conclusion, undoped and doped poly [(thiophene-2,5diyl)-co-p-methyl] benzylidene were synthesized by one pot synthesis which involved polycondensation of thiophene and p-methyl benzylidene. Both the polymers showed good solubility in common organic solvent.

Thermogravimetric analysis confirmed that both the samples have considerable thermal stability. Due to doping effect of cobalt sulphate there is slight decrease in grain size resulted decreased crystallinity and increase in the optical band gap of poly [(thiophene-2,5diyl)-co-para methyl benzylidene] which was confirmed from XRD and UV–Vis analysis. FE-SEM analysis showed interconnected structure. Cobalt sulphate doping remarkably increased surface area and porosity as observed from FE-SEM and BET. Such morphology with porous conjugated polymers is having wide applications in the fields of material science such as semiconductors, energy storage, sensing, organic electronics such as LED and solar cell.

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