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Synthesis, Characterization and Study of Effect of Irradiation on Electronic Properties of Polyaniline Composite with Metal Complex of Co (III)

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The present work reports the synthesis of PANI composite with hexamminecobalt(III) chloride metal complex as dopant via in situ oxidative polymerization by ammonium persulphate in non-aqueous DMSO medium. The dopant metal complex has been synthesized by known method and characterized by using FTIR, XRD and SEM analysis. The synthesized PANI/$[Co(NH_3)_6]$ Cl_3 composite was characterized by FTIR, XRD, UV-Vis and SEM techniques. FTIR of PANI composite showed its successful synthesis with the presence of some dopant peaks in its FTIR spectrum. XRD spectra of composite revealed its crystalline nature having almost same spectra as that of dopant metal complex with slight shift in the position of peaks. Electrical measurement of the composite was made using four probe conductivity meter and the thermal studies have been done by thermal gravimetric (TG) technique. The results showed improvement in the thermal stability of PANI composite together with increase in its conductance, thereby making it a possible future material for high temperature application purposes. Electronic properties of the composite were investigated using UV-Vis spectroscopy which revealed decrease in the energy band gap of the composite on irradiation. This is attributed to the distortion of polymer chains on exposure to radiations, which results in decrease in conjugation and hence increases in band gap energy.

Keywords: *polyaniline (PANI), PANI composite, dopant metal complex*

1. Introduction

Conducting polymers are organic polymers capable of conducting electricity that has been studied extensively and are called as the materials of 21st century. The conducting polymers which have been investigated include polyaniline (PANI), polypyrole (PPY), polythiophene (PTH), etc. New class of materials are obtained with the controlled addition of one of the components in these polymers as a dopant, a process commonly referred as doping as analogous to semiconducting technology. The reduction in the size of the dopant to nano level results in dramatic change in electrical, thermal, electronic, magnetic, optical, and other properties of polymers. In this direction polyaniline (PANI) has been studied and investigated extensively with respect to facile synthesis by chemical and electrochemical process, environmental stability, low cost, high conductivity, solubility, and chemical sensitivity[1]. It has drawn considerable attention for its wide application in microelectronic devices, photodiodes, sensors, light weight batteries, solar cells, electrochemical capacitors, corrosion capacitors, corrosion inhibitors, drug delivery and electromagnetic interference shielding materials[2-4]. Various composites of PANI with different fillers or dopants like MoO_3, MnO_3, WO_3, TiO_2, BF_3, CNTS etc. have been synthesized, characterized and explored for various possible applications[5-9]. In the same direction some of the transition metals and their complexes containing polymers have also been prepared and studied[10] and are interesting systems under consideration in various fields such as organic electronics, where PANI/metal hetero junctions are employed for electrical transport and rectification[11], as protective coatings against corrosion of metal surfaces[12-14], as redox-active catalysts for inducing chemical reactions in coordination chemistry[15,16], etc. PANI is used as a model polymer for study of the above interactions, because its backbone consists of two basic groups possessing different activity with respect to metal cations, namely the electron-rich benzenoid group and electron-deficient quinoid group[17]. The purpose of using transition metal complexes as fillers in conducting polymer matrices is to impart some desirable properties to conducting polymers. These properties include good thermal stability, good mechanical strength, crystallinity for good processibility, etc. The above mentioned properties coupled with good electrical conductivity make these nanocomposites as exciting materials for different applications. The metal complex copper(bisglycinate) has made composites suitable for high temperature application purposes[18]. The polyaniline and polythiophene composite with rare earth terbium(III) complex possess good thermal stability and fluorescence property which make them possible candidates for their technological applications as luminescent probes or light emitting diode materials[19]. Role of photoadducts using $K_4[Fe(CN)_6]$ metal complex in improving thermal, electrical and mechanical properties of PANI composite has been recently investigated by our group[20]. The present study involves the synthesis and characterization of PANI composite with a photoactive transition metal complex hexamminecobalt(III) chloride. This complex being photoactive

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undergoes redox decomposition in aqueous solution when irradiated with 254 nm light with the formation of Co^{2+} and consumption of H^+ ions according to zero order kinetics. However when irradiation is carried out in the ligand field bands, release of ammonia occurs with the quantum yield of 5.4 x 10^{-3} at 365 nm ($^1A_{1g} \rightarrow {}^1T_{2g}$ band) and 5.2 x 10^{-4} at 472 nm ($^1A_{1g} \rightarrow {}^1T_{1g}$band). The released ammonia ligands can be substituted with some new ligands of our choice. Hence, by irradiating the aqueous solution of the complex at these wavelengths in presence of some other ligand the corresponding photoadducts of the complex can be formed and subsequently doped in PANI polymer to observe the effect of incorporated ligand on the thermal, electrical, mechanical and other properties of polymer. The dopant metal complex which we have taken is having very high thermal stability and is chemically an inert metal complex. Therefore its insertion in polyaniline is expected to increase the thermal stability of the later, besides improvement in some of its other properties. Owing to water soluble nature of dopant metal complex, the synthesis of polyaniline composite has been taken in non-aqueous DMSO medium. The composite prepared has been subjected to various spectroscopic characterizations including surface morphology and also its electrical and thermal properties have been studied for its possible future applications.

2. Experimental

2.1. Materials

The chemicals used were all of analytical grade. Aniline used was supplied by Merck chemicals and was used after distillation. The other chemicals including HCl, ammonium persulphate, DMSO, cobalt (II) chloride, ammonia, hydrogen peroxide and activated charcoal were supplied by Himedia and were used as received. All solutions were prepared in triple distilled water.

2.2. Synthesis of Polyaniline (PANI)

Stable Polyaniline dispersion was prepared in non-aqueous DMSO medium by known method of oxidation of aniline monomer by ammonium persulphate $(NH_4)_2S_2O_8$. 1 ml of purified aniline was added to 10 ml of 5N solution of HCl in DMSO and the solution was cooled to a temperature of about 10°C. The solution of 1.2 g of ammonium persulphate dissolved in 10 ml of DMSO was then added drop wise to the previous cooled solution for a period of 15 min with constant stirring. The solution was left for the polymerization of aniline to take place for 12 hr at 10°C with occasional stirring. The green colored thick dispersion of PANI obtained in non-aqueous DMSO medium was isolated as precipitate by adding excess of distilled water. The green precipitate was then filtered, washed with acetone repeatedly and dried in an oven at a temperature of about 30°C.

2.3. Synthesis of dopant hexamminecobalt(III) chloride $[Co(NH_3)_6]\ Cl_3$

The synthesis of dopant hexmaminecobalt(III) chloride was carried out by standard reported method[21]. The method involves the treatment of Co(II) chloride with ammonia and ammonium chloride followed by oxidation with hydrogen peroxide in presence of charcoal as a catalyst. The labile $[Co(H_2O)_6]^{2+}$aquo-ion formed in solution upon dissolution of $CoCl_2$, reacts with ammonia to give hexamminecobalt(II) $[Co(NH_3)_6]^{2+}$ complex, which is successively oxidized by H_2O_2 to $[Co(OH)(NH_3)_5]^{3+}$. This complex is quite inert but undergoes substitution of coordinated OH^- group by NH_3 in presence of charcoal as catalyst. The ammonia buffer prevents the pH increase that would be produced by the release of OH^- ions in the substitution step. The overall reaction involved in the synthesis of the complex is as under:

$$2CoCl_{2(aq)} + 2NH_4Cl_{(aq)} + 10NH_{3(aq)} + H_2O_{2(l)} \rightarrow 2\left[Co(NH_3)_6\right]Cl_{3(s)} + 2H_2O \quad (1)$$

2.4. Synthesis of $[Co(NH_3)_6]\ Cl_3$ doped PANI composite

To precooled 1 ml distilled aniline in 10 ml of 5N HCl solution in DMSO, 1.5 g of synthesized dopant $[Co(NH_3)_6]\ Cl_3$ was added with stirring to form a dispersion as the dopant is insoluble in non-aqueous DMSO medium. To this dispersion 1.2 g of ammonium persulphate dissolved in 10 ml of DMSO solution was added drop wise at 10°C with constant stirring. The mixture was kept as such for about 12 hr at same temperature of about 10°C for polymerization reaction and simultaneous interaction between PANI chains and the dopant to take place with occasional stirring. The dispersion formed was isolated as precipitate by adding excess distilled water, filtered and washed with acetone several times. The precipitate was collected over filter paper and dried in an oven at a temperature of about 30-40°C.

2.5. Physical measurements

UV-visible spectra of PANI and that of PANI composite solution in NMP were recorded separately by UV-VIS double beam spectrophotometer (PG Instruments T80). Fourier transform infrared (FTIR) spectra were recorded on Perkin Elmer RX-1 FTIR spectrophotometer using KBr discs. X-ray diffraction (XRD) was recorded on PW 3050 base diffractometer with Cu Kα radiations (1.54060 Å). Surface morphology of the samples was taken on a Hitachi SEM Model S-3600N. Electrical measurement was made using four probe conductivity meter. Thermogravimetric analysis was carried on Universal TA instruments V4.5A in nitrogen atmosphere at a heating rate of 10 K min^{-1}. The temperature range was from ambient to 1000°C. An aluminum pan was used as a reference.

3. Results and Discussions

3.1. UV-VIS characterization

The UV-VIS spectra of PANI and PANI composite solutions prepared in NMP are shown in Figure 1a, b. The PANI spectrum shows two prominent peaks at 290 nm and 630 nm. The peaks are attributed to $\pi \rightarrow \pi^*$ transition in the benzenoid rings and $\pi \rightarrow \pi^*$ transition in quinoid rings of polyaniline[22]. In PANI composite spectrum two peaks at 335 nm and 665 nm are observed. The shift in the peaks towards higher wavelength side (red shift) as well

as increase in the intensity of peak at 665 nm suggests a decrease in the energy band gap in case of composite and increase in the number of charge carriers which can be due to interaction between dopant metal complex and the polyaniline backbone chains.

Moreover, the synthesized composite was subjected to irradiation for different intervals of time (0.0h, 0.5h, 1.0h, 1.5h) to study the effect of radiations on the PANI-metal complex composite (Figure 2). During irradiation, a blue shift in the UV-Vis spectrum of composite was observed with a gradual decrease in the λ_{max}, of composite from 635 nm to 620 nm, after different intervals of time. Due to this blue shift the band gap calculated for each time of irradiation was found to be 1.94, 1.96, 1.98, and 1.99 eV. The increase in the band gap energy of composite can be attributed to the distortion of PANI chains on irradiation due to the photochemical decomposition of filler which otherwise have held the polymer chains intact as already noted in FTIR. This distortion in PANI chains leads to the decreased conjugation and hence decreases the value of λmax (blue shift) or increases bang gap energy of the composite.

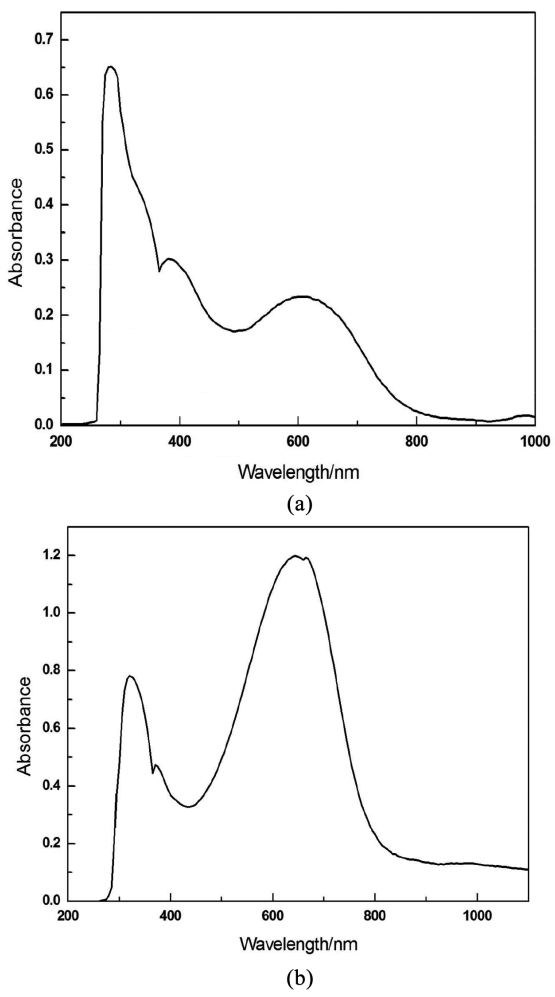


Figure 1. UV-Visible spectra of (a) pure PANI (b) PANI composite.

3.2. FTIR characterization

The FTIR spectra of PANI, dopant metal complex and PANI composite are shown in the Figure 3a-c. PANI shows a hump at 3432 cm^{-1} due to N-H stretching. The peak at 2923 cm^{-1} occurs because of aromatic C-H bond stretching. The absorption peaks in the region of 1557 cm^{-1} and 1476 cm^{-1} corresponds to quinoid and benzenoid ring vibrations respectively. The peaks at 1297 and 1241 cm^{-1} are probably associated with various C-N stretching and bending vibrations. The vibration peak at 1107 cm^{-1} is attributed to C-N double bond. The C-H out of plane bending vibration is observed at 797 cm^{-1}. The important peaks in case of dopant $[Co(NH_3)_6]Cl_3$ metal complex are observed at 3167 cm^{-1}, 1618 cm^{-1}, 1327 cm^{-1} and 830 cm^{-1}. While the first three peaks are assigned to various N-H stretching vibrations of complexed NH_3, the latter one is because of rocking vibration of NH_3 molecule. The FTIR spectrum of PANI composite is very much similar to that of pure PANI, with some shift in the position of peaks and the presence of some new dopant peaks. Vibrational frequencies in PANI composite are observed at 3114 cm^{-1} for combined

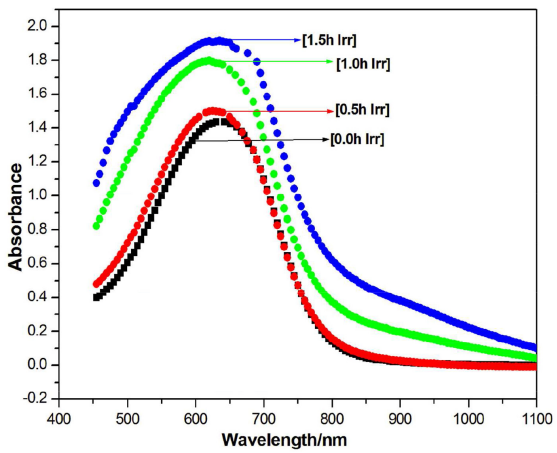


Figure 2. UV-Visible graph of composite after different intervals of irradiation.

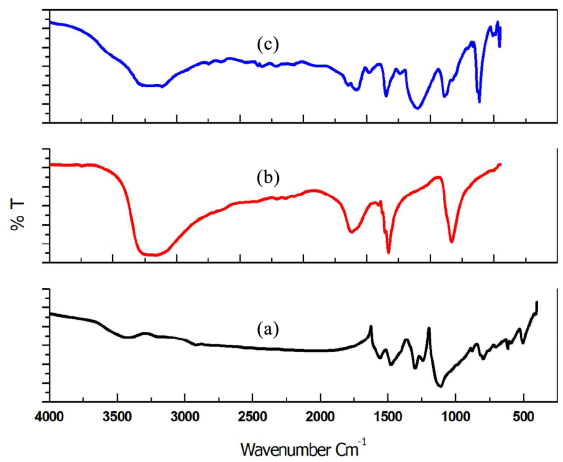


Figure 3. FTIR spectra of (a) pure PANI (b) dopant metal complex (c) composite.

N-H stretching frequencies of complexed NH_3 and that of PANI with a decreased intensity. The peak at 1574 cm^{-1} for quinoid ring vibration shows a significant shift while as the peak at 1481cm^{-1} for benzenoid ring stretching remains almost unchanged in the composite. This suggests a possible interaction that might have occurred between the quinoid ring and the dopant metal complex. The peaks at 1238 cm^{-1} and 1099 cm^{-1} corresponds to C-N single bond and double bond stretching. The insertion of dopant metal complex into the PANI is evident by the presence of some dopant peaks in the FTIR spectrum of PANI composite with some shift in their position. The peaks observed at 1645 cm^{-1} and 1347 cm^{-1} in the composite are due to N-H stretching vibrations of complexed NH_3 of dopant metal complex. These peaks appear at 1618 cm^{-1} and 1327 cm^{-1} respectively in pure dopant metal complex. The observed peak at 830 cm^{-1} in pure dopant because of rocking vibration of NH_3 molecule shifts to 888 cm^{-1} in PANI composite. Therefore from the discussion of FTIR of pure dopant metal complex and that of PANI composite, successful synthesis of PANI composite is proved. Also, since there occurs some shifting of PANI peaks due to the addition of metal complex, which indicates van der Waals type of interaction between them.

3.3. XRD characterization

The XRD data was analyzed using Powder X software. Figure 4a-c, represents the diffraction pattern of pure PANI, dopant Co complex and PANI composite with the metal complex. The peaks are indexed by characteristic Miller indices. The XRD spectrum of pure PANI shows a broad hump at 2θ value of 20° which indicates its amorphous nature. The dopant metal complex shows some sharp peaks characteristic of a crystalline substance and these peaks matches well with the JCPDS -International centre for diffraction data, ICSD No 001694, page No.705-736, suggesting that the prepared metal complex is pure with monoclinic C2/m (12) structure. The XRD pattern of PANI-metal complex composite resembles with that of dopant Co complex with peaks at same position or with some slight shift in their position. This indicates crystalline nature of composite. The lattice parameters calculated for the dopant metal complex after refinement are a = 12.49, b = 12.42 and c = 21.47 with α =γ = 90° and β = 112.96°, whereas for the PANI composite the value of various lattice parameters are a = 12.50, b = 12.29 and c = 21.68 with α =γ = 90° and β = 113.63°. The different parameters of PANI and PANI composite calculated from XRD are shown in Table 1 and Table 2 respectively.

3.4. SEM characterization

The surface morphology of pure PANI, metal complex and PANI composite have been investigated using SEM analysis and are shown in Figure 5a-c. The SEM picture of PANI shows uniform morphology with amorphous layer like structure. The dopant metal complex shows compact morphology thereby supporting the XRD. The SEM image of PANI composite reveals that the dopant metal complex particles are dispersed in PANI matrix which also justifies the successful composite formation.

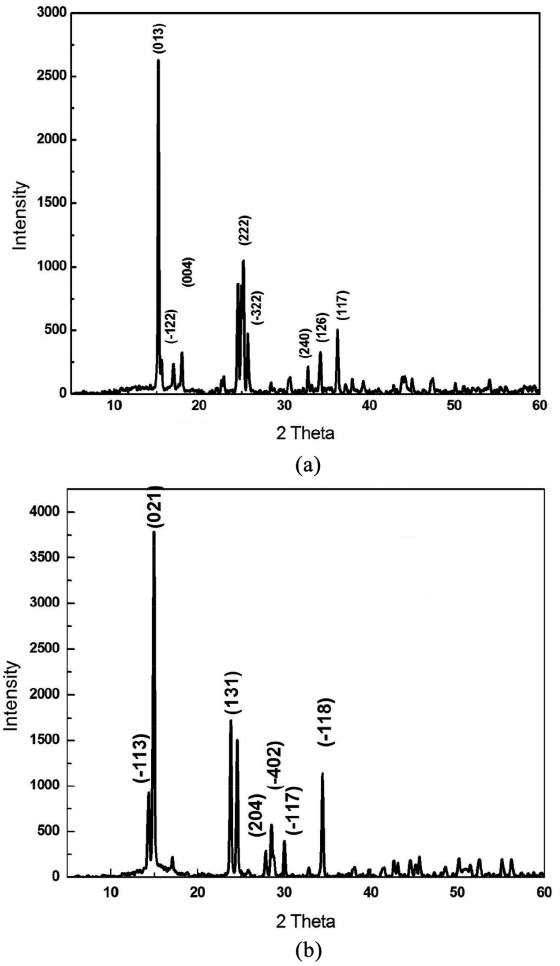


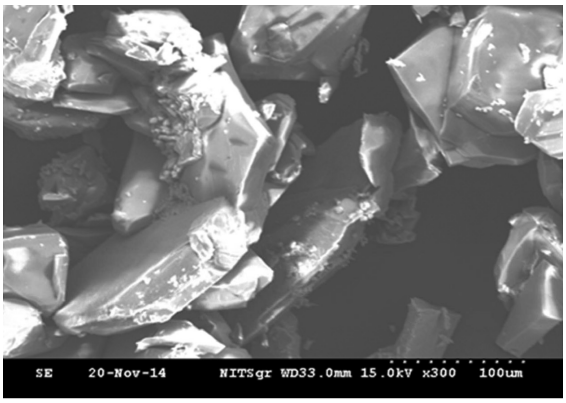
Figure 4. XRD of (a) dopant metal complex (b) PANI composite.

Table 1. Evaluated parameters from XRD data of dopant metal complex.

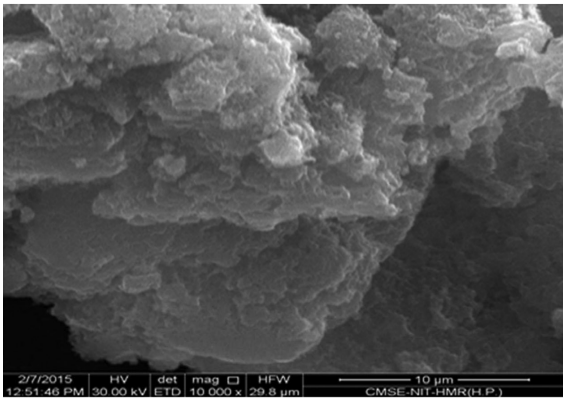
H	K	L	2θ (exp.)	2θ (cal.)	2θ (diff.)	d (exp.)	d (cal.)	Intensity
0	1	3	15.212	15.208	0.004	5.81964	5.82110	2638.30
-1	2	2	16.982	17.010	-0.029	5.21705	5.20837	236.04
0	0	4	17.963	17.933	0.029	4.93425	4.94227	324.79
2	2	2	25.199	25.190	0.009	3.53136	3.53255	1054.90
-3	2	2	25.714	25.742	-0.027	3.46168	3.45809	474.86
2	4	0	32.794	32.752	0.042	2.72876	2.73213	214.24
1	2	6	34.247	34.258	-0.012	2.61624	2.61537	326.74
1	1	7	36.267	36.289	-0.022	2.47498	2.47353	505.72

Table 2. Evaluated parameters from the XRD data of PANI composite.

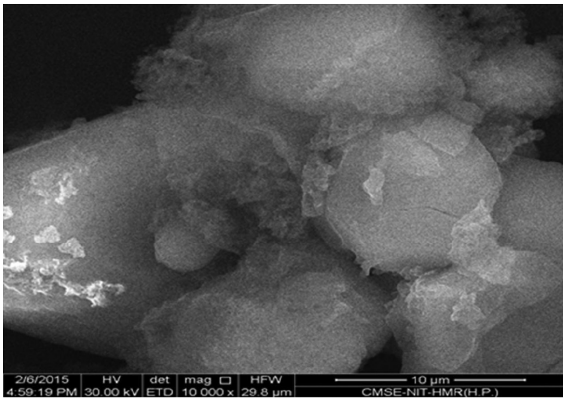
H	K	L	2θ (ex.)	2θ (calc.)	2θ (diff.)	d (exp.)	d (calc.)	Intensity
-1	1	3	14.356	14.343	0.014	6.16458	6.17044	926.22
0	2	1	14.970	14.953	0.017	5.91316	5.91989	3784.60
1	3	1	23.841	23.863	-0.022	3.72922	3.72585	1721.74
2	0	4	27.888	27.931	-0.042	3.19659	3.19183	285.67
4	0	2	28.540	28.539	0.001	3.12508	3.12514	575.38
-1	1	7	30.038	30.037	0.001	2.97252	2.97265	395.37
-1	1	8	34.438	34.415	0.024	2.60212	2.60386	1142.70



(a)



(b)



(c)

Figure 5. SEM images of (a) dopant metal complex (b) pure PANI (c) PANI composite.

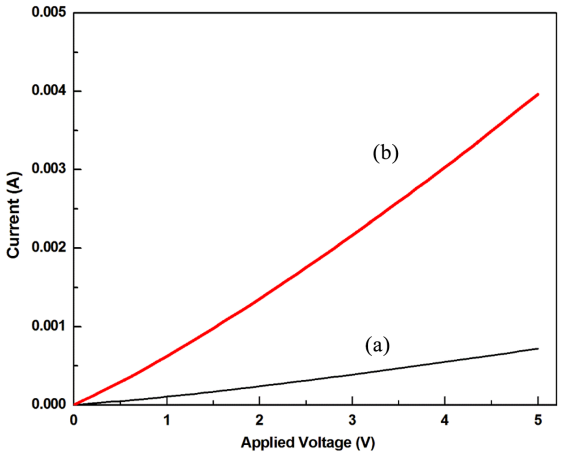


Figure 6. I-V curves of (a) pure PANI (b) PANI composite.

3.5. Conductivity/I-V measurement

Figure 6a, b shows the I-V graphs of PANI and PANI composite. The polyaniline has semiconducting nature as already known, having conductance of 12 mS (Figure 4a). In case of PANI, the conduction occurs because of the presence of some conjugational defects like polarons and bipolarons, in addition to electrons and trapped ions. However the addition of metal complex has increased its conductance by about 6 orders in magnitude to about 75 mS (Figure 4b). The increase in conductance can be explained on the basis of generation of some additional energy levels associated with metal complex in between HOMO-LUMO energy gap thereby decreasing band gap and increase in the number of charge defects. This fact is also supported by UV-Vis spectra of PANI and PANI composite. Thus it is evident that the inserted metal complex has increased the conductance of PANI composite.

3.6. Thermal analysis

The TGA curve of pure PANI and PANI composite is shown in Figure 7a, b. The TG curve of PANI shows an early weight loss due to release of moisture within the layers. The curve then shows stability up to 350˚C, wherefrom it undergoes a fast decomposition of about 95-98%, which lasts up to 600˚C. The TG of PANI doped with $[Co(NH_3)_6]Cl_3$complex shows improvement in thermal stability by about 200˚C. The thermogram shows initial

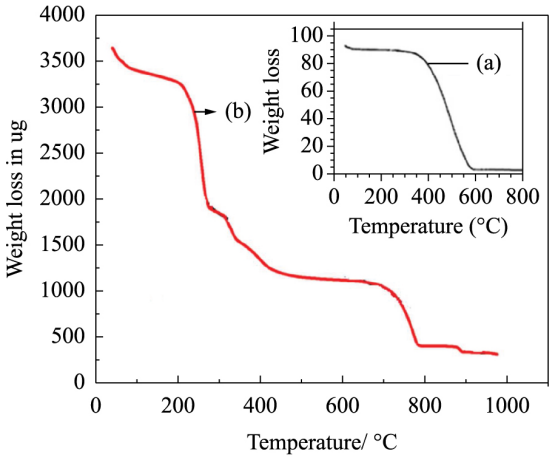


Figure 7. TGA curves of (a) pure PANI (b) PANI composite.

decomposition of 8% from ambient up to 200°C, due to release of moisture. This decomposition leads to further continuous weight loss of 60% up to 500°C, which may be due to loss of C, H and N moieties. After 500°C the thermogram runs parallel to X-axis, showing stability up to 700°C, wherefrom it undergoes further weight loss of about 20% which may be because of release of dopant moieties. The thermogram shows some amount of residue even at 800°C, which reflects the thermal stability of PANI composite with $[Co(NH_3)_6]Cl_3$ have increased significantly.

4. Conclusion

Successful synthesis of metal complex and PANI composite with metal complex has been proved by FTIR spectra. XRD study shows crystalline structure of metal complex, which is retained by the composite. SEM images reveal dispersion of metal complex particles in PANI matrix. UV-Vis spectroscopy revealed increase in energy band gap of composite on irradiation due to distortion of polymer chains. The electrical measurement shows increase in conductance of composite as compared to PANI. Thermal analysis shows increase in the thermal stability of PANI composite by about 200°C than that of pure PANI. The material synthesized can be used for high temperature application purposes.

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