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Thermal stability of CdS/ZnS nanoparticles embedded conducting polyaniline nanocomposites

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ABSTRACT

Nanostructured CdS and ZnS have been synthesized by chemical precipitation method using DMF as stabilizing agent. Nanocomposites of conducting polyaniline with CdS/ZnS nanoparticles have been synthesized by chemical oxidation polymerization method using ammonium persulphate (oxidant) and sulfuric acid (dopant). A series of the nanocomposites have been synthesized by varying the weight percentage of CdS/ZnS (5, 10, 15, 20%) in the polymerization of aniline (monomer). Crystalline nature and size of the particles have been analyzed by X-ray diffraction study. The particle size was found to be less than 10 nm which has been confirmed from TEM images. Thermal stability of polymer nanocomposites has been analyzed by TGA and corresponding thermal kinetic parameters were calculated. As the weight percentage of CdS/ZnS nanoparticles increases in the polyaniline (PANI) matrix, half decomposition temperature increases gradually and activation energy also increases. These results indicate that the polymer nanocomposites are thermally more stable as compared to that of pure PANI.

Keywords: conducting polymer, polyaniline, nanocomposites, thermal stability.

INTRODUCTION

Inorganic semiconductors like silicon, gallium arsenide have been the backbone of the semiconductor industry for the last four decades. Now a days with the emerging field of conducting polymers along with the advantages of nanotechnology, such organic (semi) conductors are proved very promising materials in electronic, optoelectronic devices, gas sensors etc. Among different conducting polymers, polyaniline (PANI) has occupied the most important place in the family of conducting polymers due to good stability in air, simplicity in doping, improved electronic properties and high conductivity in the doped state [1]. But when

PANI is taken in the composite form, its properties are altered from those of basic materials. Also nanocomposites of PANI with inorganic materials show dramatically changes in the thermal, mechanical and electrical properties of the overall composites.

The thermal stability of PANI has been investigated by many researchers in present years and the results have shown that PANI base has a very good thermal stability and has higher thermal activation energy whereas PANI doped with protonic acids are significantly less stable [2]. Therefore along with better conductivity, several researchers have shown that thermal stability of PANI could be improved by combining PANI with polystyrene latex [3], multiwalled carbon nanotubes [4], ZnO nanoparticles [5], graphite [6], MCM-41 (mesoporous silica) [7] etc.

Inorganic semiconductors CdS/ZnS nanoparticles are the most promising II-VI compound materials used in various applications like sensors, optoelectronic devices and in solar cells. Studies on PANI-CdS and PANI-ZnS nanocomposites have been reported by many researchers [8-11] and focused on electrical conductivity, but little is known about the thermal properties of such nanocomposites. Along with electrical conductivity, thermal stability of the polymers plays important role to modify the polymer properties to be used for advanced applications. Hence thermal stability of conducting PANI and its composites has great importance. This paper presents the thermal study of PANI-CdS and PANI-ZnS nanocomposites in terms of TGA (Thermo-Gravimetric Analysis) and throws light on various thermal kinetic parameters like thermal activation energy (Ea), change in entropy (ΔS), free energy(G) and half decomposition temperature (Ts). Again, it has been shown in the present article that the enhancement of the thermal stability of PANI composite was achieved by increasing the weight percentage of CdS/ZnS in the polymer matrix.

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 CdS/ZnS nanoparticles

0.1 M cadmium salt solution [Cd^{++}] was made by dissolving Cadmium Nitrate in double distilled water and 0.1M Na_2S solution [S^{--}] was also made in double distilled water. From these stock solutions, 100 ml of Cadmium Nitrate solution was mixed with specific amount of DMF and stirred for 10 minutes. Then 100 ml Na_2S solution was added in the mixture dropwise with constant stirring for 1 hour. This results in a cloudy yellow solution. This solution was kept overnight. Later on it was washed with distilled water several times to eliminate the unreacted molecules. The obtained nanoparticles were filtered and dried in vacuum oven at $60^{O}C$ for 8 hours. Dry yellow powder of CdS nanoparticles was obtained. The same procedure was used to synthesize ZnS nanoparticles for which zinc acetate was used as a precursor. Powdered CdS and ZnS thus obtained was used to synthesize PANI /CdS and PANI-ZnS nanocomposites.

Synthesis of Polyaniline (PANI)

In 100 ml solution of 0.4 M aniline in 1M sulfuric acid, 100 ml of 0.5 M solution of ammonium persulphate was added dropwise with constant stirring at room temperature at normal condition. After completion of the oxidant addition, stirring was continued for further 2 hours to insure completion of the reaction. During polymerization, the sequence of coloration of the reaction mixture was light blue, blue green and finally greenish black precipitate. This color indicates that the product was in conducting emeraldine salt form. The reaction mixture was kept overnight. Then it was filtered, washed with distilled water until the filtrate become colorless and finally with methanol to remove the impurities and oligomers. The product was dried in vacuum oven at 80^{O}C for overnight. A greenish black salt of polyaniline (PANI) was obtained.

Synthesis of PANI-CdS and PANI-ZnS nanocomposites

PANI-CdS/ZnS nanocomposites have been synthesized by the same procedure used for polyaniline. Powder of synthesized CdS/ZnS nanoparticles in different weight percentage (e.g.5%) with aniline was added in the aqueous aniline solution followed by the dropwise addition of oxidant. By varying the percentage of CdS/ZnS i.e.5%, 10%, 15% and 20%, a series of nanocomposites have been obtained. Same synthesis conditions were maintained for all composites as that of pure PANI to compare the results.

Characterizations

X-RD spectra of all samples were taken on Philips PW -1700 , Automatic X-ray diffractometer using Cu-Kα radiation of wavelength 1.544 Å, continuous scan of 2^o/ min., with an accuracy of 0.01 at 35 KV and 20 mA. TEM micrographs of synthesized CdS and ZnS were taken on Transmission Electron Microscope PHILIPS model- CM200 with resolution 2.4Å. TGA thermograms of all samples were recorded on Perkin- Elmer Diamond TGA/DTA in argon atmosphere at a heating rate of 10^{o}C/ min. TGA profile were taken over the temperature range of 30-1000^{o}C.

RESULTS AND DISCUSSION

The broadness of the diffraction peaks as obtained in XRD spectra (fig. 1a) gives the direct consequence of the reduced particle size and crystalline phase of synthesized CdS and ZnS indicating the nanocrystallites were cubic with (111), (220) and (311) planes. PANI showed two peaks at 2θ =20^o and 25^o and has an amorphous nature [12]. A nanocomposite show the greater crystallinity due to the addition of CdS/ZnS in PANI matrix as compared to pure PANI and shows the peaks related to CdS/ZnS with increasing concentration in PANI matrix as seen from figure 1(b) and 1(c).

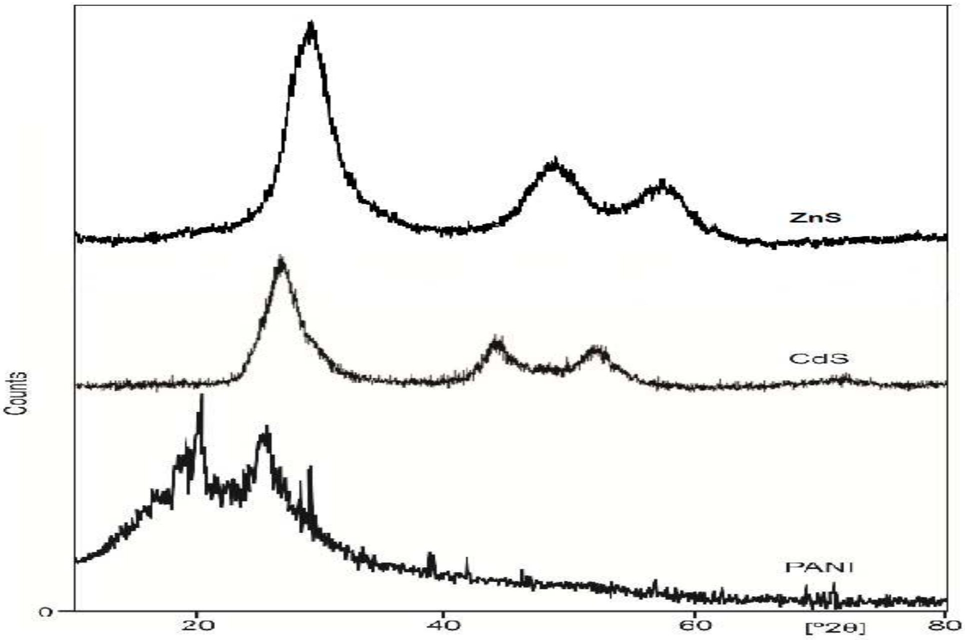

Fig.1 (a) XRD pattern of PANI, CdS and ZnS

From these figures, we can observe broad diffraction peaks for all composites indicating the presence of very small size crystallites. Again, it can be seen that the nanocomposites show crystalline as compared to that of pure PANI due to uniform dispersion of the nanoparticles in the polymer matrix. The cristallinity of the nanocomposites is dominated by polymer matrix.

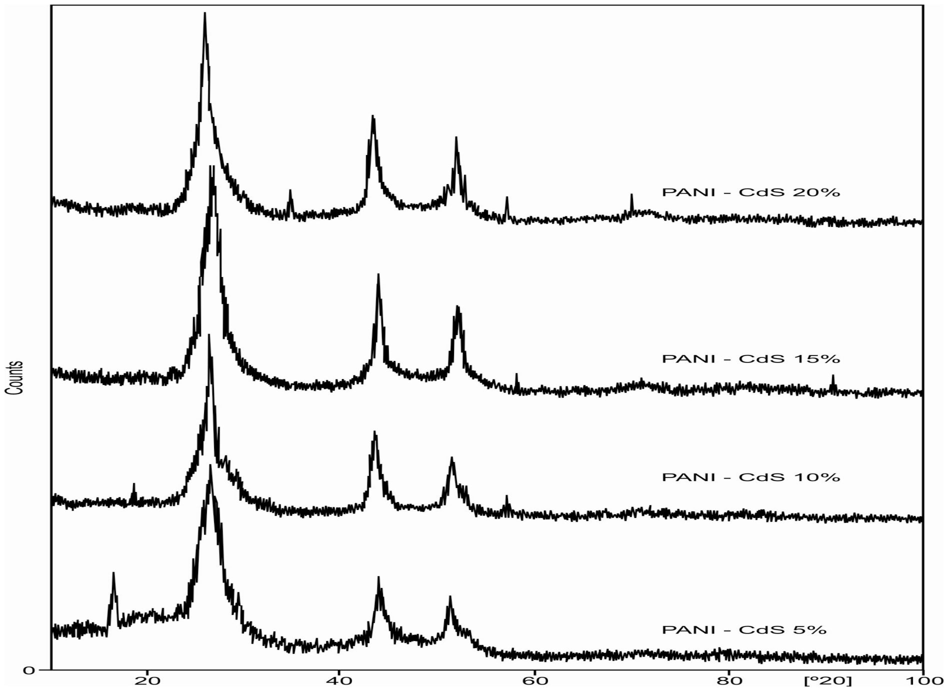

Fig.1 (b) XRD pattern of PANI-CdS nanocomposites

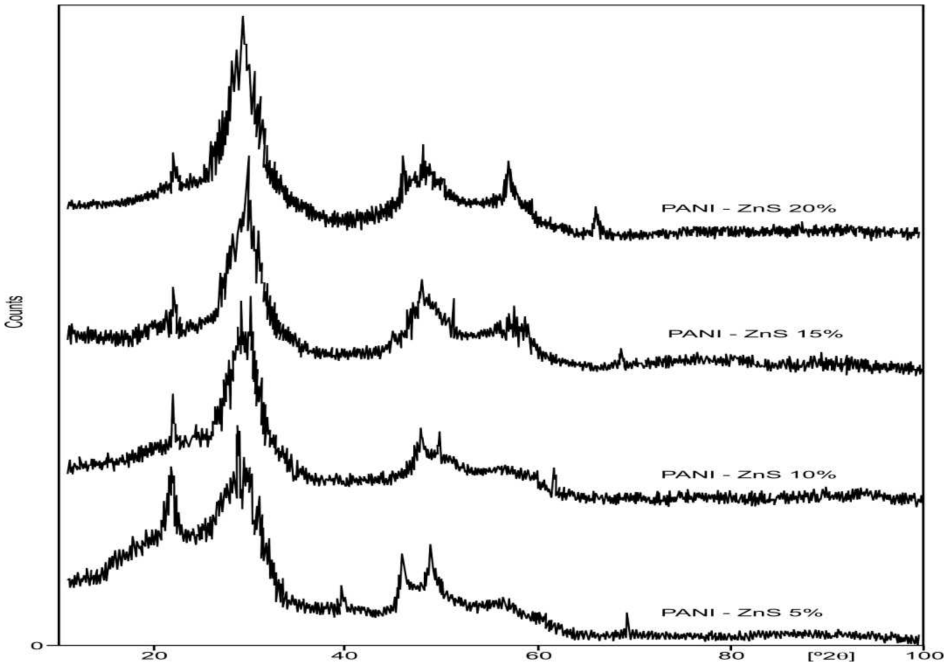

Fig.1 (c) XRD pattern of PANI-ZnS nanocomposites

Figure 2(a) and 2(b) represent the TEM micrographs of synthesized CdS and ZnS respectively, which clearly indicate the formation of particles of size less than 10 nm. Fine nanoparticles of

ZnS are clearly seen in the images as compared to that of CdS. These images reveal the formation of nanoparticles of ZnS and CdS as prepared by precipitation method and clearly shows fine particles of ZnS as compared to that of CdS.

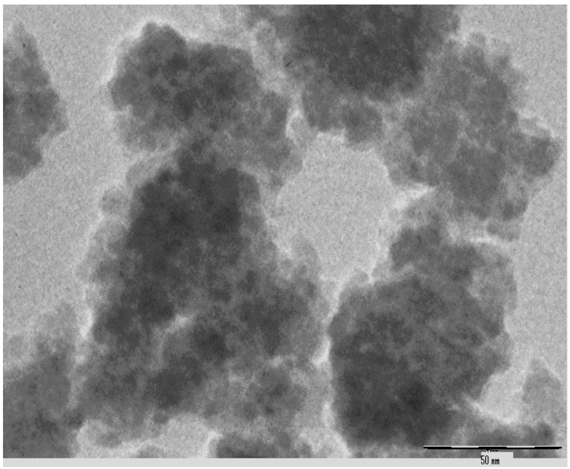

Fig.2(a): TEM image of synthesized CdS (scale bar 50nm)

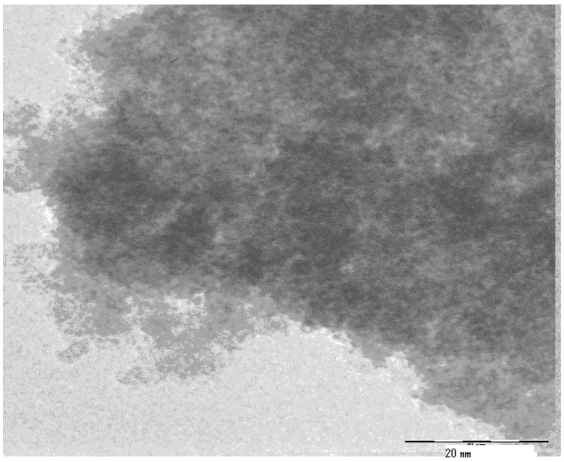

Fig.2(b): TEM image of synthesized ZnS (scale bar 20nm)

TGA thermograms of PANI, CdS and ZnS are shown in fig.3 (a). From this figure, it is observed that about 64 % of DMF capped CdS and ZnS are stable up to 1000°C. The initial loss in weight may be due to moisture and amount of DMF present in the material. Small variation observed in the TG thermogram may be due to the variation in the particle size of CdS and ZnS. TG thermogram of pure PANI emeraldine salt shows three major stages for the weight loss up to 800°C. The first weight loss of 13% at around 120°C is due to evaporation of moisture [13]. This agrees with the results reported earlier (0.78 water molecule per monomeric unit [14]). The second stage of weight loss starting at 150°C up to 350°C represents the evaporation and degradation of sulphuric acid group and low molecular weight polymers [15]. From 350°C onwards, degradation of skeletal PANI chain structure takes place [16] up to 800°C in which almost 91% mass loss is observed.

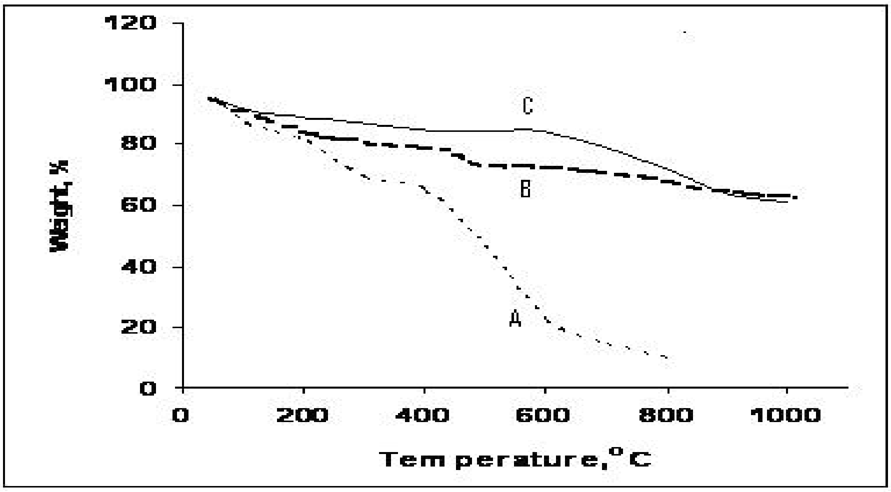

Fig. 3 (a): TG thermograms of (A)PANI (B)ZnS and (C) CdS

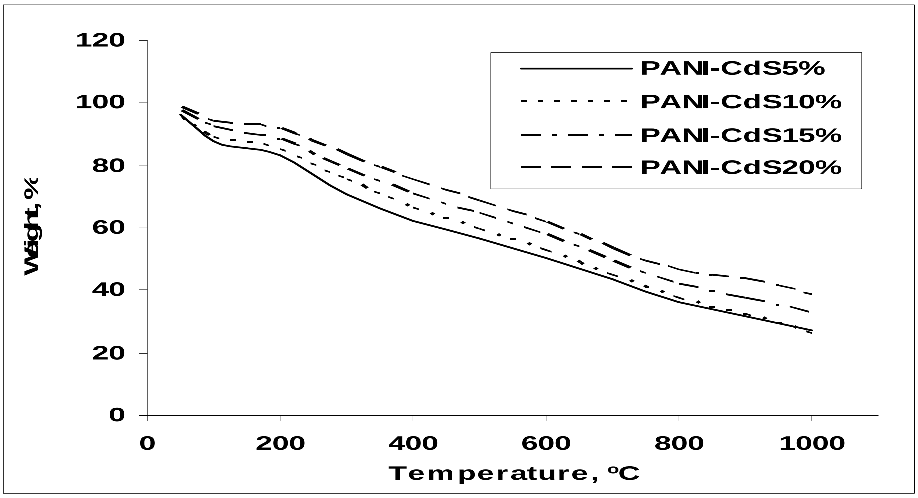

Fig.3 (b): TG thermograms of PANI-CdS nanocomposites

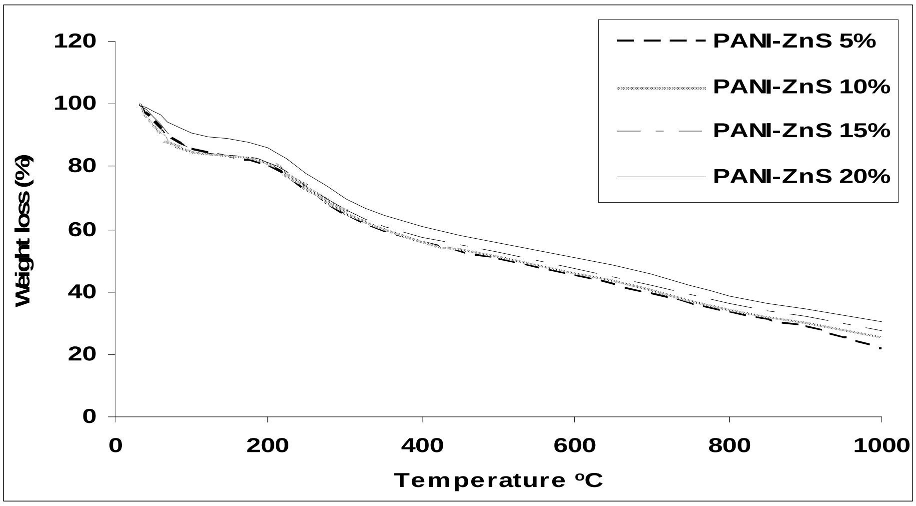

Fig.3 (c): TG thermograms of PANI-ZnS nanocomposites

The TGA thermograms of PANI-CdS and PANI-ZnS nanocomposites containing different weight percentage of CdS and ZnS are shown in fig.3 (b) and fig.3 (c) respectively. It was observed that PANI-CdS nanocomposites containing 5%, 10%, 15% and 20% weight of CdS shows weight loss of 12 to 7% at 120^{o}C which is less than PANI. Similarly it shows second stage of degradation between 150-300^{o}C. Above 300^{o}C, polymer degradation takes place slowly up to 1000^{o}C unlike pure PANI which almost degrades at 800^{o}C. Similar behaviour in the degradation process was also observed for PANI-ZnS nanocomposites. PANI degrades rapidly between 350 to 600^{o}C but the composites decompose slowly from 400 to 1000^{o}C. A remarkable feature of PANI nanocomposites which is absent in PANI salt is that they leave behind a considerable amount of residue even after 1000^{o}C which may be the respective metal sulfide which are undegradable below 1000^{o}C, while PANI shows almost 91% weight loss at 800^{o}C. Also it was observed that as the weight % of CdS/ZnS nanoparticles increases in PANI matrix, this residue goes on increasing. As the weight % of CdS increases in the PANI matrix, the % residue goes on increasing which is 26% for PANI-CdS 5% and 39% for PANI-CdS 20% nanocomposites while for PANI-ZnS series, the percentage residue increases from 22 to 30% as ZnS content increases from 5% to 20%. Conclusively, the TGA studies point out the inference that, PANI-CdS and PANI-ZnS nanocomposites are thermally more stable than PANI salt. Again if we compare the results of both the series, it was found that PANI-CdS nanocomposites are thermally more stable than PANI-ZnS nanocomposites. In order to compare the relative thermal stability of nanocomposites and pure PANI, the kinetic parameters and the temperature T_s at which half weight loss occurred are recorded in table 1.

"Sharp - Wentworth method" [17] has been employed for the determination of thermal parameters like thermal activation energy, change in entropy and free energy change of thermal degradation. While calculating these parameters, for the sake of calculations, the central linear region between 400-700°C was considered for all samples which is the main region for polymer degradation. The activation energy (E_a) for the thermal degradation process was calculated using equation,

$$\log [(dc/dT)/(1-c)] = \log A - E_a/2.303\ kT \qquad \text{----- (1)}$$

where, c is the fractional weight loss at temperature T
$A= \alpha / \beta$, is the pre-exponential factor
E_a can be calculated from the slope of the plot between log [(dc/dT)/ (1-c)] and 1/T.

The values of entropy of activation (ΔS) and the free energy change (G) were calculated using the following Equations [18],

$$\Delta S = 2.303 \log (Ah/ kT_s) \qquad \text{------ (2)}$$
$$G = E_a - T_s (\Delta S) \qquad \text{------ (3)}$$

where, h - Planck's constant,
k - Boltzman constant.
T_s - Temperature at half weight loss

From table 1, it is observed that the activation energy and the temperature at which half weight loss occurs are higher in composites as compare to pure PANI salt. PANI degraded half of its original weight at about 786 K while this temperature increases to 877 K for 10% composite and up to 1014 K for composite containing 20% weight of CdS.

Table1: Kinetic parameters for PANI and nanocomposites.

Polymer composites	Ea (KJ/mole)	Δ S (J/K)	G (KJ/mole)	Ts (K)
PANI	9.5	-43.16	24.4	786
PANI-CdS 5%	11.94	-43.08	48.34	845
PANI-CdS 10%	12.52	-42.86	50.11	877
PANI-CdS 15%	13.152	-43.12	52.39	910
PANI-CdS 20%	13.71	-43.20	57.5	1014
PANI-ZnS 5%	10.1	-42.7	40.85	745
PANI-ZnS 10%	11.79	-43.4	45.64	780
PANI-ZnS 15%	13.21	-43.1	47.70	800
PANI-ZnS 20%	11.7	-42.9	49.8	888

Similarly for PANI-ZnS 20% composite, this value increases to 888K. Since the temperature at which half weight loss occur is one of the main criteria for the thermal stability of the polymer composites, we can conclude that composites of PANI with CdS and ZnS nanoparticles are thermally more stable than pure PANI. Also it is observed that, as the weight % of nanoparticles increases in the PANI matrix, the values of activation energy and T_s increases which indicates the existence of strong interaction at the interface of PANI and embeded nanoparticles and increased thermal stability of the composites.

The negative values of entropy (ΔS) indicates that the polymer has the more ordered structure as the entropy is the measure of disorder, the disorder is less, the structure is more order.

CONCLUSION

A series of polyaniline–CdS/ZnS nanocomposites have been synthesized by chemical oxidation polymerization method. Broad XRD peaks and TEM micrograph of CdS and ZnS confirms the nanosized particles. From XRD spectral analysis, it is observed that as the percentage of CdS/ZnS increases in PANI matrix, composites show ordered structure. TGA study reveals that thermal stability of PANI is greatly improved after the composite formation with such nanoparticles. TGA curves of nanocomposites show similar nature as that of PANI with three significant degradation steps. Increased in thermal activation energy and temperature of half weight loss inferred the thermal stability of nanocomposites as compared to pure PANI.

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