Synthesis and Characterization of Cd/$CuSeO_3$ Nanocomposites

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Abstract: Cd/$CuSeO_3$ nanocomposites were prepared by a facile microwave assisted hydrothermal method using cadmium acetate dihydrate, copper acetate dihydrate and sodium selenite as precursors. The XRD pattern reveals that the material is a composite material Cd/$CuSeO_3$ and the average size of the nanocrystallite is found to be 15 nm. XRD, SEM, EDX and FTIR studies confirm the morphology and composition of Cd/$CuSeO_3$ nanocomposites. The optical band gap energy of the material was estimated using Kubelka-Munk relation. PL spectrum of the sample exhibits a sharp, intense peak at 430 nm. Thermogravimetric analysis (TGA) was carried out to analyze the stability of the material.

Index Terms **- Nanocomposite, Microwave, hydrothermal, optoelectronics.**

I. INTRODUCTION

Nanocomposites are multiphase materials consisting of at least two phases in nanoscale with dissimilar properties with one dispersed in other forms a three-dimensional network to achieve required improvement in properties such as catalytic, electronic, optical, cytotoxicity, chemical as well as thermal stabilities, etc. [1,2]. These materials exhibit unique electrical mechanical, and optical properties making them valuable for applications in areas like photo-imaging, optics and sensor design, information storage, patterning, and antimicrobial coatings[3]. Materials with desired characteristics can be created by mixing materials with suitable properties. This has gained considerable interest in the field of oxide materials. The powerful surface interactions that exist between intimately packed nanoparticles within the oxide systems is generally recognized that the obtained characteristics of composite materials may not be deemed as just a facile superposition of individual properties Thus, the goal behind the synthesis of multicomponent materials has always been to integrate the improvements in the characteristics of various phases to enhance and broaden their applications[4].

Transparent conducting oxides (TCOs) are electrically conductive materials with comparably low absorption of electromagnetic waves within the visible region of the spectrum. They are used in optoelectronic devices such as solar cells, displays, optoelectronic interfaces and circuitries[5]. TCO has been received considerable attention from researchers due to their remarkable low resistivities and high transmittance in the visible region[6]. Oxy chalcogenides optically transparent in the visible light region, although simple chalcogenides are transparent only in the IR region[7]. Cadmium selenite nanoparticles are transparent fluorescent n-type material having a wide direct bandgap and high photosensitivity. Materials that are transparent to visible light are useful to develop transparent electronics, UV optoelectronics, and integrated sensors. In this article, we tried to prepare a nanocomposite of oxy chalcogenide Cd/$CuSeO_3$ using a microwave- assisted hydrothermal method. The microwave-assisted synthesis is a unique and simple technique which offers fast and rapid processing of materials with higher reproducibility. It has emerged as an economic tool for particle size reduction. The ability of microwaves to react with the molecules directly and generation of heat in a quick span of time has been found suitable for the synthesis of nanocomposites.[2]

2. EXPERIMENTAL

2.1. Synthesis of Cd/$CuSeO_3$ nanocomposites

Cd/$CuSeO_3$ nanocomposites were synthesized by microwave irradiation through an aqueous medium. Cadmium acetate dihydrate, copper acetate dihydrate, and sodium selenite of analytic reagent grade in 1:1:1 molar ratio was used as precursors to prepare cadmium and copper selenite nanocomposites. These chemicals were dissolved in distilled water and stirred well using a magnetic stirrer. The as prepared solution is irradiated with microwaves until the water gets evaporated[8]. The colloidal precipitate thus formed is washed several times using double distilled water and acetone and filtered. The formed product was allowed to dry naturally. As-prepared nanocomposites were annealed for one hour at 100^0C to improve ordering.

2.2. Instrumentation

The powder XRD pattern for the as prepared sample was done using Bruker AXS D8 Advance diffractometer with Copper target and Cu-Kα (λ=1.5406 Å) radiation. Energy Dispersive X-ray EDX analysis was done using Oxford XMX N EDX analyser. Scanning electron microscope (SEM) was employed for morphological study using Hitachi S-3400 N operated at 3kV. The surface morphology was investigated and recorded by means of a Thermo Nicolet**,** Model;6700 Fourier Transform Infrared Spectrometer. The UV-Vis absorption spectral studies were carried out using VARIAN 5000 UV-Vis-NIR Spectrophotometer in the spectral region of 200 and 800 nm. The photoluminescence spectra of the samples were recorded with VARIAN ECLIPSE Fluorescence Spectrophotometer. Thermogravimetric (TG) and Differential thermo gravimetric analysis (DTG) for the air-dried sample was performed on a Q600 SDT Thermal analyser at a heating rate of 20 °C min-1

3. RESULTS AND DISCUSSION

Grey colored Cd/$CuSeO_3$ nanocomposites were successfully prepared by a simple microwave driven hydrothermal method.

3.1. Powder X-Ray Diffraction (XRD) Analysis

The reflected ray measurements were made within the angular range 2θ from 20° to 80° is shown in fig.1. The XRD pattern of Cd/$CuSeO_3$ nanocomposite shows diffraction peaks at 2θ of 12.47°, 22.37°,25.72°, 26.48°, 29.451°, 30.66°, 32.39°, 33.32° ,35.7°, 39.56°, 46.53°, 41.83°, 52.6°, 56.57°, 61.3°, 73.03° which can be attributed to the crystal planes (011), (012), (-112), (130), (102), (032), (140), (210), (023), (051), (221), (231), (152), (311), (025), (350), and (106). This crystal planes are matching with the crystal planes of monoclinic crystals of $CdSeO_3$ (ICSD PDF 01-082-1208), with the space group P21/c (14) having unit cell parameters a= 5.70840 A°, b=12.82830 A°, c=8.58600 A°, β=101.21°, Z=8, mol weight =239.37, volume [CD]= 616.75 (A°), Dx= 5.15. In addition, the XRD patterns of Cd/$CuSeO_3$ nanocomposite powders show some diffraction peaks at 29.03°, 32.943°, and 56.5°, which can be attributed to the orthorhombic $CuSeO_3$ crystals (PDF 01-082-1208), with the space group Pnma (62) having unit cell parameters a= 5.4770A°, b= 6.152A°, c=7.307A°, α=β=γ=90°.

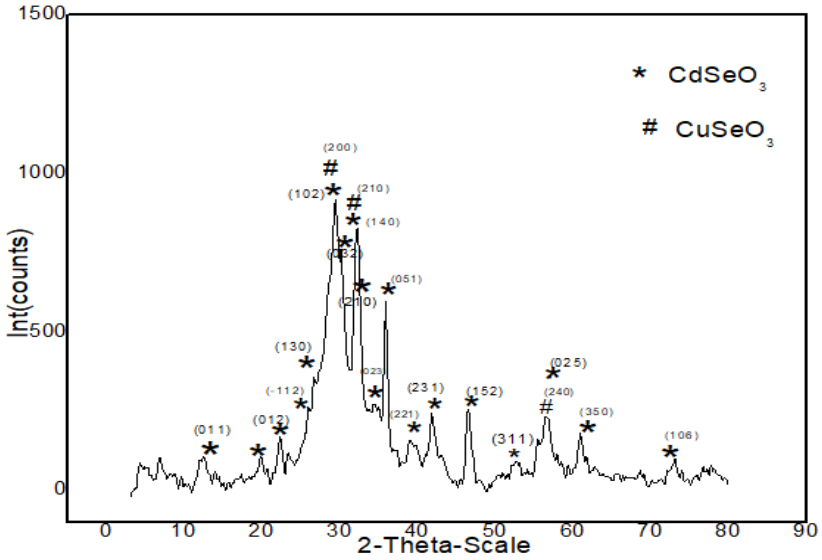

Fig.1. XRD pattern of as prepared Cd/$CuSeO_3$ nanocomposites

XRD pattern of the sample showed the peaks of $CuSeO_3$ in addition to the peaks of $CdSeO_3$. From the results, it was inferred that the sample is $CdSeO_3$ and $CuSeO_3$ nanocomposites with some percentage of $CuSeO_3$ mixed into the $CdSeO_3$ lattice. The orthorhombic peaks of $CuSeO_3$overlap with some of the monoclinic peaks of $CdSeO_3$. The peaks of $CdSeO_3$ and $CuSeO_3$ are denoted by asterisks and sash symbols, respectively in fig.7.2. The broad diffraction peaks in the diffractogram indicate the nanocrystalline nature. The average crystallite size was calculated by Debye-Scherrer formula[9-14]. The size of $CdSeO_3$ nanoparticles in the nanocomposites is 15nm and the size of $CuSeO_3$ nanoparticles is 14nm.

3.2. Energy Dispersive X-Ray Spectroscopy (EDX) Analysis

EDX analysis was done to analyze the composition of elements quantitatively and to find the chemical identity of the elements present in the nanocomposite. Fig.2. shows the EDX spectrum of Cd/$CuSeO_3$ nanocomposites. The EDX studies on the as-prepared nanocomposites confirm the presence of Cd, Cu, Se and O. No trace of other elements is observed. From the EDX analysis, it is clear that the obtained products are pure cadmium and copper selenite nanocomposites.

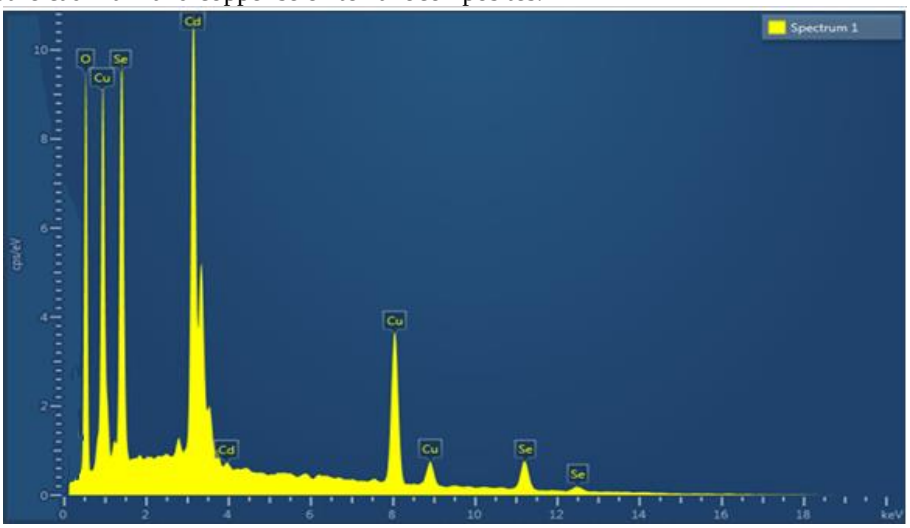

Fig. 2. EDX spectrum of as prepared Cd/$CuSeO_3$ nanocomposites

3.3. Scanning Electron Microscope (SEM) Analysis

Scanning electron microscope (SEM) was employed for morphological study to analyze the morphology and the growth features of the as-prepared nanoparticles. SEM images at different magnifications of as-prepared cadmium and copper selenite nanocomposites are shown in Fig.3. which shows that the particles are agglomerated. The pictures confirm the formation of bright, spherical Cd/$CuSeO_3$ Quantum dots.

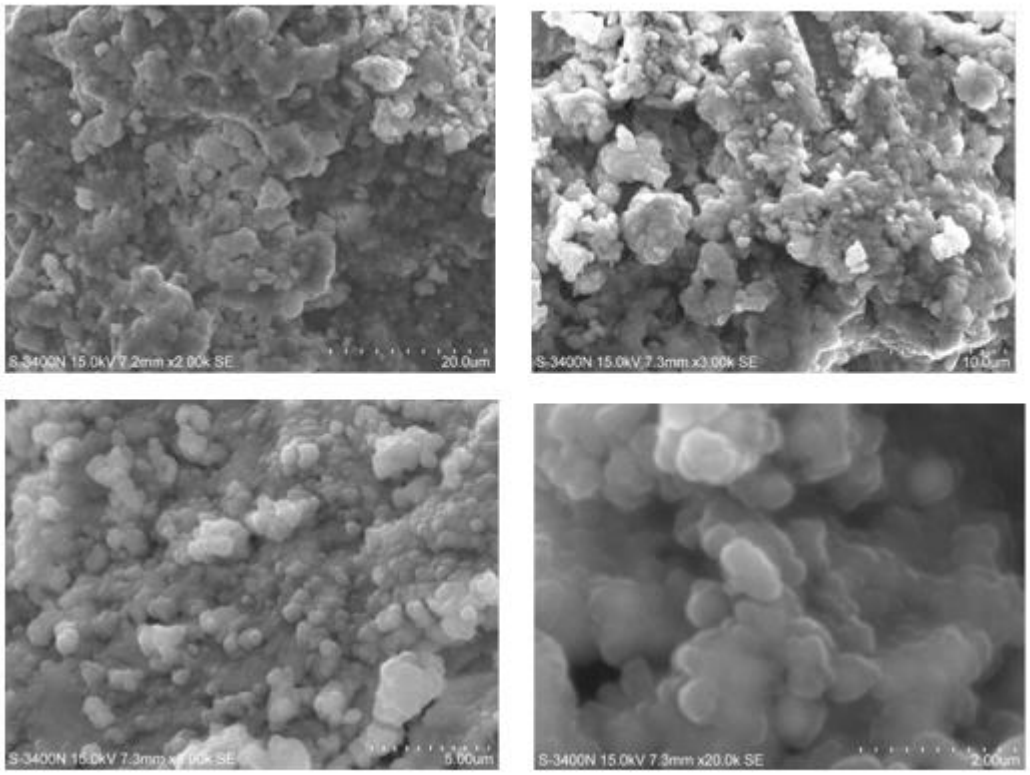

Fig. 3. SEM micrograph of as prepared Cd/$CuSeO_3$ nanocomposites

3.4. FTIR Spectroscopy Analysis

The infrared molecular spectrum of as-prepared Cd/$CuSeO_3$ nanocomposites is shown in the fig.4. In the FTIR spectrum of Cd/ $CuSeO_3$ nanocomposites, the presence of SeO_3 is confirmed by its characteristic deformation peaks at 467 $cm^{-1}$and 498 cm^{-1} and asymmetric stretching at 752 cm^{-1}[15-17]. Considerable splitting in the band confirms the crystallinity of the material. The weak peaks at 1041.5 cm^{-1} and 1079.1 cm^{-1} attributed to C-O stretching. The strong peak at 1417 cm^{-1} is assigned to O-H bending could be due to the absorbed water in the surface of Cd/ $CuSeO_3$ nanocomposites.

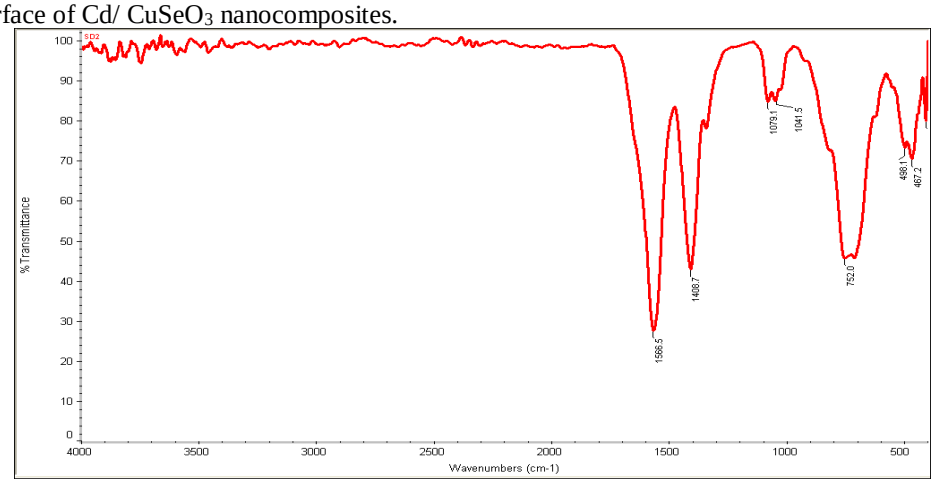

Fig. 4. FTIR spectrum of as prepared Cd/$CuSeO_3$ nanocomposites

3.5. UV-Vis absorption spectroscopy Analysis

Fig.5(a). shows the absorption spectrum of Cd/ $CuSeO_3$ nanocomposites in the spectral region of 200 nm to 800 nm. An absorption edge is observed at around 440 nm. Maximum absorption is observed in the UV region. The increase in absorbance at the lower energy around 700 nm region originates from the indirect bandgap of the semiconductors. Maximum absorption is observed in the ultraviolet regions. The diffused reflectance spectrum (Fig.7.8.) shows a sharp reflectance peak around 600 nm. Transparency is observed in the visible region. This could be a potential candidate for solar cells and window materials.

Kubelka-Munk equation was used to calculate the optical energy gap [21-23]. Fig.5(b) shows the Diffused reflectance spectrum of Cd/ $CuSeO_3$ nanocomposites. Fig.6 shows the plot of $(F(R)hv)^n$ vs. hv. Straight lines were drawn on the linear portion of the curve and stretched out to intercept the hv axis to get the bandgap of the sample. From the Kubelka–Munk plot the optical energy bandgap Eg= 2.9 eV for direct allowed transition and Eg=1.75eV for indirect allowed transition were estimated. Cd/$CuSeO_3$ nanocomposites are interesting indirect bandgap semiconductors which have potential application in several optoelectronic devices[24]. The wide bandgap semiconductors are efficient emitters in the blue to the ultraviolet spectral range and are suitable candidates for light-emitting laser diodes. Having an indirect bandgap close to the bandgap necessary for solar cells Cd/$CuSeO_3$ nanocomposites are potential candidates for solar cells as well.

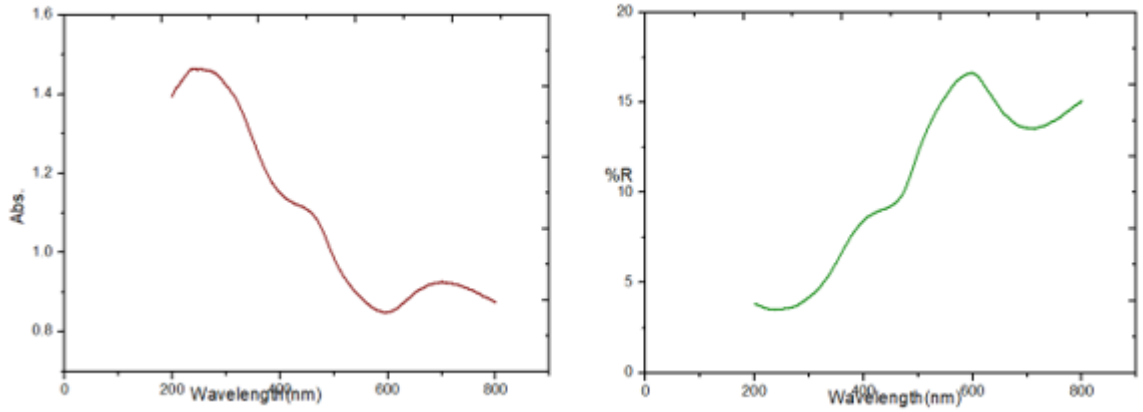

Fig. 5. a) UV-Vis Absorption spectrum and b) Diffused reflectance spectrum of as prepared Cd/CuSeO$_3$ nanocomposites

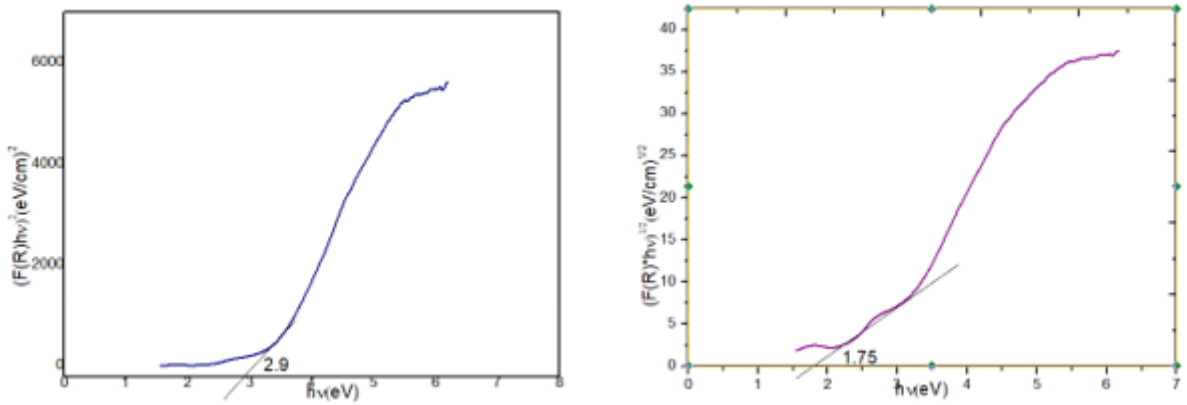

Fig. 6. Kubelka-Munk plot for a) direct transition and b) indirect transition of as prepared Cd/CuSeO$_3$ nanocomposites

3.6. Photoluminescence (PL) Analysis

Fig.7. shows the photoluminescence spectrum of as-prepared Cd/CuSeO$_3$ nanocomposites. The photoluminescence spectrum of Cd /CuSeO3 nanocomposites prepared by the hydrothermal process excited at an excitation wavelength 380 nm exhibits a sharp, intense peak at 430 nm and a weak peak at 830 nm. It is evident from the PL spectrum that the emission peak at 430 nm can be assigned to the surface trap induced fluorescence which involved the recombination of electrons trapped inside the hole in the valence band[25]. The absorption and emission edge are a clear indication of the visible light response of the particles indicating that the material can be used for various fluorescence applications. In addition, the material is a promising biological label[26].

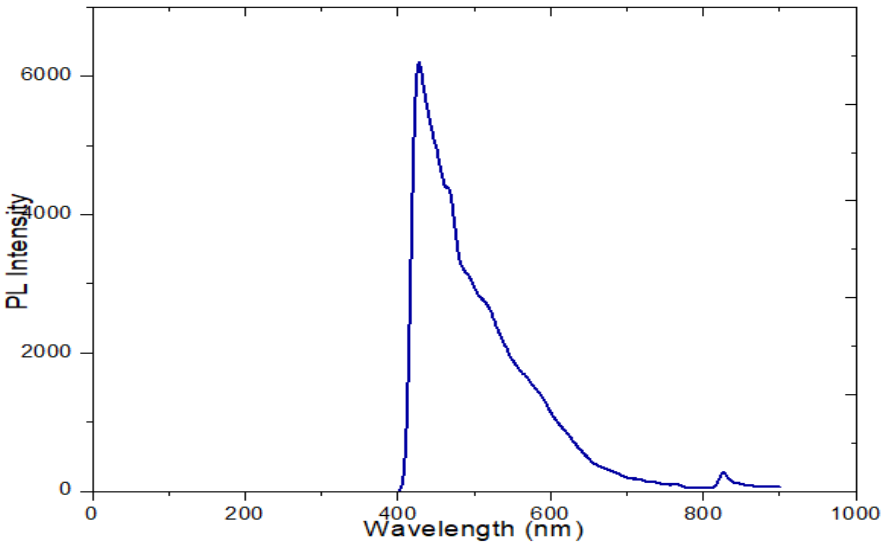

Fig.7. Photoluminescence spectrum of as prepared Cd/CuSeO$_3$ nanocomposites

3.7. Thermal Analysis

The thermogravimetric curve obtained by heating the as-prepared Cd/CuSeO$_3$ nanocomposites in nitrogen flow from 25–900°C at the rate of 20°C/min is shown in Fig.8. From the thermogram, Initially, the material lost 13.37% mass till 74.42^{0}C through endothermic reaction, which could be due to the removal of absorbed water molecules. Then there is a mass loss of 10.36% from 224.47 to 254.26^{0}C through the endothermic reaction. From 254.26^{0}C to 614.50^{0}C the material remains stable indicating the stability of the material. From 614.5^{0}C to 720^{0}C the material suffers a loss of 11.89% mass, could be due to the sublimation of SeO_2 anion in the form of SeO_2 gas at high temperature as reported in the earlier literature[27-29].

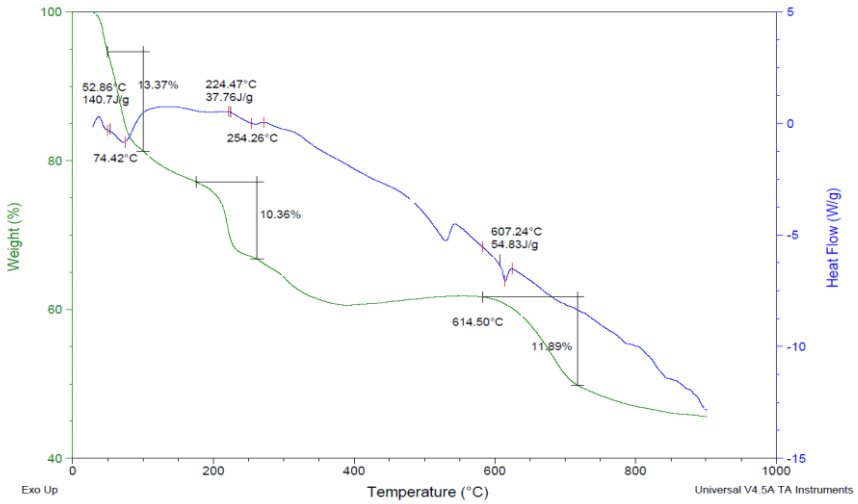

Fig.8. TGA curve of as prepared Cd/$CuSeO_3$ nanocomposites

4. CONCLUSION

Cd/$CuSeO_3$ nanocomposites were successfully prepared by a simple hydrothermal method using a microwave oven. The prepared materials were characterized and confirmed that the material is in nanoscale by XRD analysis. EDX analysis results confirm the presence of Cd, Cu, Se, and O in the prepared samples. The FTIR studies confirm the presence of functional group SeO_3. The optical direct and indirect bandgap energy of the material was estimated to be 2.8 eV and 1.7eV using the UV-Visible spectrum. PL spectrum of the samples exhibits a sharp, intense peak at 430 nm. From the results obtained it is evident that this material has good optical qualities and is well suited for optoelectronic devices.

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