Systematic long-term investigation on Cu_2ZnCdS_4 wide band gap semiconducting materials for optics and luminescence applications

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Copper Zinc Cadmium Sulfide (Cu_2ZnCdS_4) semiconducting material compound synthesized using a new economic beneficial route. Copper sulfate, zinc sulfate, cadmium sulfate and thiourea salt solutions were utilized for Cu_2ZnCdS_4 compound formation. Basic characteristics like pH value, electrical conductivity, concentration measurements were investigated for several hundred samples. Optics transmittance was investigated by UV – Vis spectrophotometer within the 350 to 950 nm range. Photo luminescence measurement was examined by using photo–fluorometer. Optic properties of Cu_2ZnCdS_4 compound were investigated through photo-calorimeter measurements including mixed wavelength bands. The real time investigated noteworthy results from several hundred samples are presented and discussed.

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1. Introduction

Copper sulfide (CuS) semiconducting material showed many excellent physiochemical properties. Due to its important properties many researchers worked and still are working on CuS, Cu2S, metal ions doped CuS, Cu2S and its related many materials compositions. Small sized copper sulfide (Cu_2S) nanoparticles with a core size of less than 5.5 nm showed some unique physicochemical characteristics and medical-kinetic properties. Many world-wide researchers attracted on this material compound due to important bio-medicine applications of Cu_2S nano particles. Some biomedicine properties such as molecular imaging and tumor therapy were reported on Cu_2S compound in recent years [1]. Further photo-thermal ablation of tumor cells using Cu_2S material were reported in recent literature. In recent research work authors developed CuS material compounds and suggested for the successive photo-thermal ablation of cancer cells using a new type of agent [2].

In a recent review article reported in detail about CuS nanoparticles applications in the medical field such as antitumor and antibacterial activities. Further the clinical merits and demerits of CuS nanoparticles were also discussed [3]. This review research article mainly deals with the phototherapy of bacterial infections and cancer treatment using CuS nano materials. Preparation and analysis of CuS nano material using the polyol method was also reported more recently [4]. Wen Gao et al. reported the Cu_2S nanoparticles acts as a photo-thermal switch [5]. Few years before CuS nanoparticles prepared by Two-phase colloidal method was also reported [6].

In a recent report, the synthesis of Cu and CuS nanoparticles using urtica dioica leaf extract was reported. Thermal effects on CuS nanoparticles were discussed in that research work. Basic measurements such as XRD, UV spectroscopy, SEM and EDX were utilized to justify the fabricated copper sulfide nanoparticles physical, surface, elemental and optic properties. In that

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report the improved crystallinity of the copper sulfide nanoparticles was achieved at the annealing range in-between 180-500 °C respectively. The particle size of the Cu nano material heat treatment at approximately 500 degrees showed 28 nm and copper sulfide nanoparticles heat treatment at 250 °C showed around 6 nm respectively [7]. In a recently reported research articles, the various copper and sulfur compositions of CuS related compounds such as CuS, Cu_7S_4, Cu_9S_5, $Cu_{7.2}S_4$, and Cu_2S were successfully synthesized by the hydrothermal method with the same surface morphology. In this research article with respect to CuS stoichiometry with the same morphology showed the enhanced energy storage capacity [8-10].

The structural property and optic properties of Cu doped ZnS nano materials was reported in a recent research article. In that work, a team of scientists discovered that copper (Cu^+) ions doped zinc sulfide (ZnS) nanocrystals showed the unusual photo-chromic characteristics. Under the UV light and visible photon radiation, this Cu:ZnS compound changes the creamy white colour to dark gray colour. The most important and interesting thing is after one minute time interval the true initial creamy white colour regained from the excited state dark gray colour when the excitation source is turned off. The colour retained time interval reduced from minutes to microseconds when this material merged with aqueous solutions. This team reported that this Cu:ZnS crystals showed never-before-seen photochromatic behavior [11]. Cu incorporated ZnS (Cu:ZnS nanoparticles) material were prepared by using the co-precipitation method. The properties of Cu:ZnS nanoparticles were analyzed for mono-grain solar cell application [12]. Visible wavelength photon assisted photocatalysis process by using Cu-ZnS nanomaterials was reported in recent literature [13]. Influence of Copper inclusion in Cadmium Sulfide material and its multiple properties such as crystalline, optic, electrical and surface properties were reported in recent year [14].

Chalcogenide semiconducting materials have gained much interest in materials research and products development field for past several years due to its remarkable semiconductor properties. Among these materials the zinc sulfide (ZnS) and various metal ions doped ZnS materials has much applications because it has a large tunable band gap from 2.1 electron volt to 3.68 eV respectively. Also, these compounds show very good transmittance and photo luminescence characteristics in visible region. We have reported several research articles in various journal forum for the past 16 years related to these semiconducting materials and its noteworthy applications [15-18]. In this research article we conducted a detailed research investigation on the ionic concentration effects of different positive ion sources like Cu^+, Zn^{2+}, Cd^{2+} and S^{2-} on a novel Cu_2ZnCdS_4 quaternary compound liquid state synthesis for various scientific applications. Total sample reactions were conducted and those properties measured at real time. The observed results on Cu_2ZnCdS_4 quaternary compound liquid state properties tailoring trends are presented and discussed in detail.

2. Experiment

For this experiment hydrated copper sulfate $CuSO_4.XH_2O$ (0.1 M), hydrated zinc sulfate $ZnSO_4.XH_2O$ (0.1 Molarity), $CdSO_4.XH_2O$ (0.1 Molarity) (+) ionic concentrations and thiourea $CS(NH_2)_2$ (0.1 Molarity) sulfur (-) ionic source concentrations were maintained constant for total Cu_2ZnCdS_4 compound synthesis. For every synthesis 0.1 M each positive ions and negative ion solutions was maintained in a sonicated small size micro filler plastic pipette and solutions drop wise added gently in the cuvettes and beakers. The constant pressure applied to the micro filler for ejecting each chemical solution drop almost constant. Basic equipments like pH meter, electrical conductivity meter (EC), TDS meter were utilized for real time Cu_2ZnCdS_4 compound formation nature analysis and the measurements continued for several hundred bath concentrations. Especially for all compound reactions the two different pH meter instrumentations were utilized for the perfect calibration and research results reproducibility comparison. To get most precise results there are three different standardized pH buffer solutions such as (i) pH:4.00, (ii) pH:6.86 and (iii) pH:9.18 were utilized systematically for each sample real time investigation. Prior to each liquid sample investigation both the pH and EC meters well cleaned by double filtered water, isopropyl alcoholic standard cleaning solution. Further the meters gentle cleaned by filter sheet.

Both EC and pH meters were maintained inside the distilled water for one minute before each concentration measurement to avoid contamination related instruments measurement corrections. The TDS meter used to investigate the Cu_2ZnCdS_4 compound liquid state formation ionic concentration nature. Further we compared the TDS value and EC value difference for the entire synthesized liquid state Cu_2ZnCdS_4 compound. The real time UV-Vis transmittance measurements were conducted in the λ range between 350 nm to 950 nm for all the Cu_2ZnCdS_4 sample concentrations. The Photo-colorimeter study at various monochromatic wavelengths and polychromatic mixed wavelengths bands were conducted for all of Cu_2ZnCdS_4 material compound formation at real time under ambient atmosphere. Further the room temperature real time photoluminescence properties of Cu_2ZnCdS_4 compound were investigated by digital photo-fluorometer instrumentation using two different 5840 Å and 5113 Å primary filters and three different secondary filters respectively.

3. Results and discussion

3.1. Cu_2ZnCdS_4 compound real time pH value change with respect to various concentration

The pH value real time change studies on Cu_2ZnCdS_4 compound were successfully investigated for several hundred samples. Some important noteworthy results are presented in fig. 1 (a-d). The observed systematic results showed the pH value raise and falls are mainly based on each individual elements composition and compound formation characteristics. The pH value decreased when the $CS(NH_2)_2$ drop wise concentration change (from 1 drop to 3 drops) during real time Cu_2ZnCdS_4 compound formation and the result shown in the following fig. 1a. Further pH started to increase when the $CS(NH_2)_2$ concentration at 4 drops and the result shown in the fig.1a.

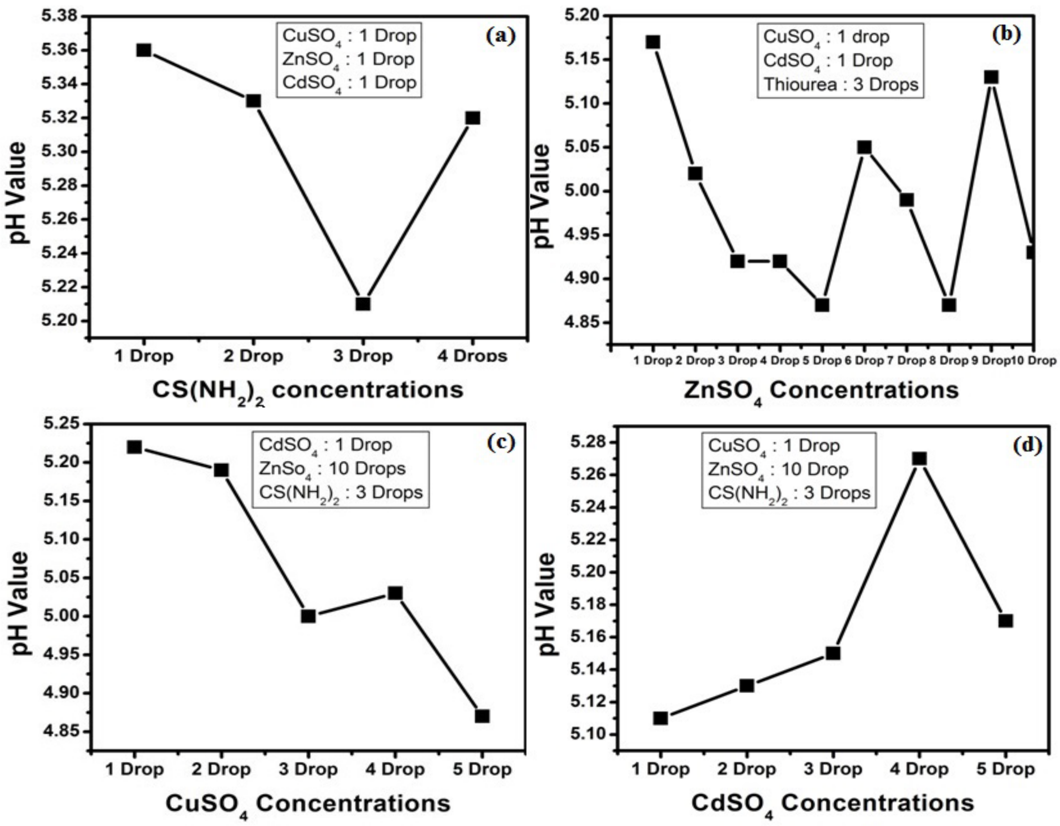

Fig. 1. (a-d) The real time pH change value studies on Cu_2ZnCdS_4 compound.

The pH value drastically changed when the $ZnSO_4$ drop wise concentration change from 1 to 10 drops during Cu_2ZnCdS_4 compound formation and the observed results shown in the following fig. 1b. The pH value decreased steadily when changing the $CuSO_4$ drop wise concentration change during real time Cu_2ZnCdS_4 compound formation and the result shown in the following fig. 1c. The pH value increased steadily when changing the $CdSO_4$ drop wise concentration change (1 drop to 4 drops) during real time Cu_2ZnCdS_4 compound formation and the result shown in the following fig. 1d. Further pH value decreased when $CdSO_4$ concentration 5 drops.

3.2. Cu_2ZnCdS_4 compound real time Electrical conductivity (EC) value change with respect to various concentrations

The real time Electrical conductivity (EC μs/cm) change value studies on Cu_2ZnCdS_4 compound were successfully investigated for several hundred samples. Some most important noteworthy results are presented in fig. 2 (a-d). The observed systematic results showed the EC value raise and falls are mainly based on each individual positive and negative elements composition and compound formation nature. The EC value decreased when the $CS(NH_2)_2$ drop wise concentration change from 1 to 4 drops during Cu_2ZnCdS_4 compound formation and the result shown in the following fig. 2a. The EC value increased when the $ZnSO_4$ drop wise concentration change from 1 to 10 drops during Cu_2ZnCdS_4 compound formation and the result shown in the following fig. 2b. The EC value change of $ZnSO_4$ concentrations and $CS(NH_2)_2$ concentrations showed opposite trend. The EC value drastically increased when the both $CuSO_4$ and $CdSO_4$ drop wise concentration independently change from 1 to 5 drops during Cu_2ZnCdS_4 compound formation and the result shown in the following fig. 2 c-d.

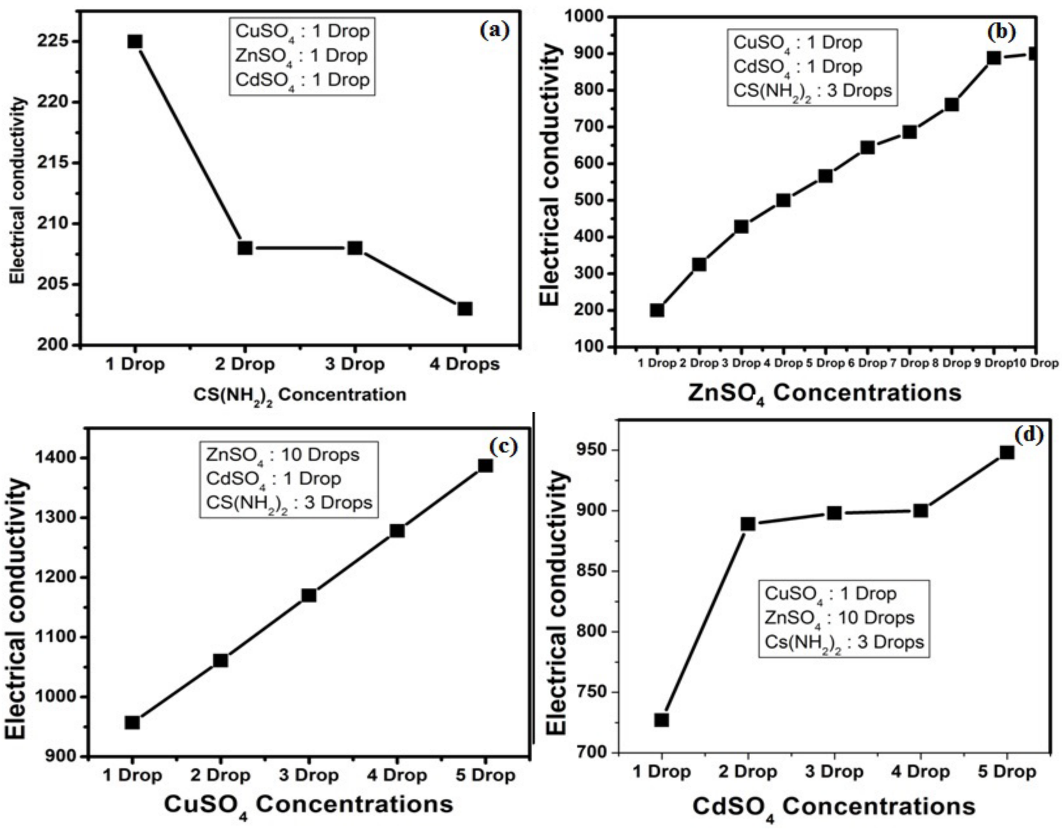

Fig. 2. (a-d) The real time Electrical conductivity (EC μS/cm) change value studies on Cu_2ZnCdS_4 compound.

3.3. Cu_2ZnCdS_4 compound real time TDS value change with respect to various concentrations

The real time TDS value studies on Cu_2ZnCdS_4 compound were successfully conducted for several hundred liquid samples. Few most interesting noteworthy results are showed in the fig. 3 (a-d). The examined systematic results showed the TDS value raise and falls are mainly based on each individual positive and negative elements composition and compound forming duration nature. The TDS value decreased much when the $CS(NH_2)_2$ drop wise concentration increase from 1 to 4 drops during Cu_2ZnCdS_4 compound formation. The observed results are shown in the following fig. 3a. The TDS value increased from 400 to 1800 when the $ZnSO_4$ drop wise concentration increase from 1 to 10 drops during Cu_2ZnCdS_4 compound formation. Fig. 3(c-d) shows the measured results and we found the gradual increment of $ZnSO_4$ (1 to 10 drops) and $CuSO_4$ concentration (1 to 5 drops), the TDS meter showed similar increasing trend. The TDS value also increased for $CdSO_4$ concentration 1 to 2 drops (1450 ppm to 1800 ppm), maintaining steady TDS value when $CdSO_4$ from 2 to 4 drops (1800 ppm) and further increasing to 5 drops leads again TDS value increasing (1850 ppm).

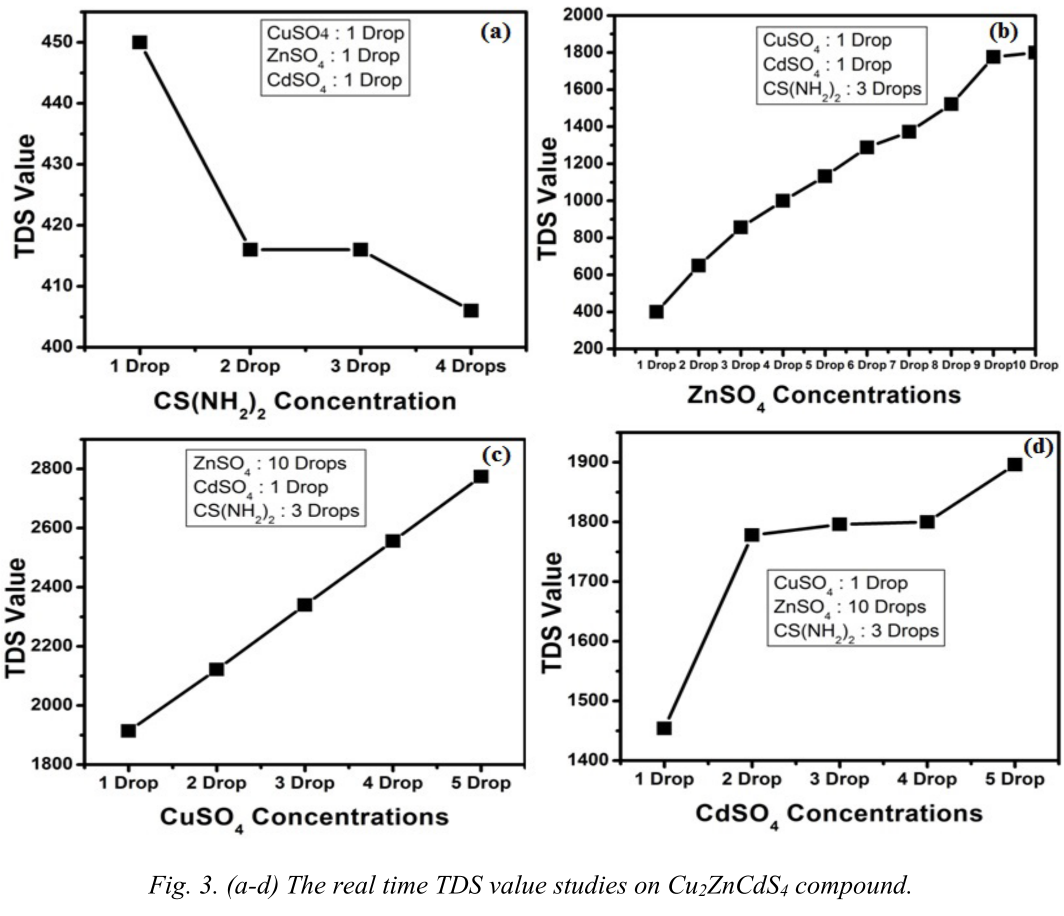

Fig. 3. (a-d) The real time TDS value studies on Cu_2ZnCdS_4 compound.

3.4. Cu_2ZnCdS_4 compound real time photo-colorimeter wavelength band response

Photo-colorimeter wavelength band responses during Cu_2ZnCdS_4 compound real time formation were investigated for several hundred samples. The input wavelengths are violet, violet-blue, blue-green, green-blue, bluish green, green, yellow and red. Fig. 4 (a-d) shows the photo-colorimeter each wavelength band responses during Cu_2ZnCdS_4 compound real time formation with respect to various sulfur source $CS(NH_2)_2$, various metal ion sources such as $CuSO_4$, $ZnSO_4$ and $CdSO_4$ respectively. Fig. 4 a. shows the photo-colorimeter wavelength band responses for various $CS(NH_2)_2$ concentration from 1 drop to 5 drops (all other element compositions fixed) during Cu_2ZnCdS_4 compound real time formation. During Cu_2ZnCdS_4 compound formation each

$CS(NH_2)_2$ drop increment shows a new photo-colorimeter wavelength band response. Fig. 4 b. shows the photo-colorimeter wavelength band responses for various $ZnSO_4$ concentrations from 1 drop to 10 drops (all other element compositions fixed) during Cu_2ZnCdS_4 compound formation. During Cu_2ZnCdS_4 compound formation, each $ZnSO_4$ drop increment shows a new photo-colorimeter wavelength band graph theory like response.

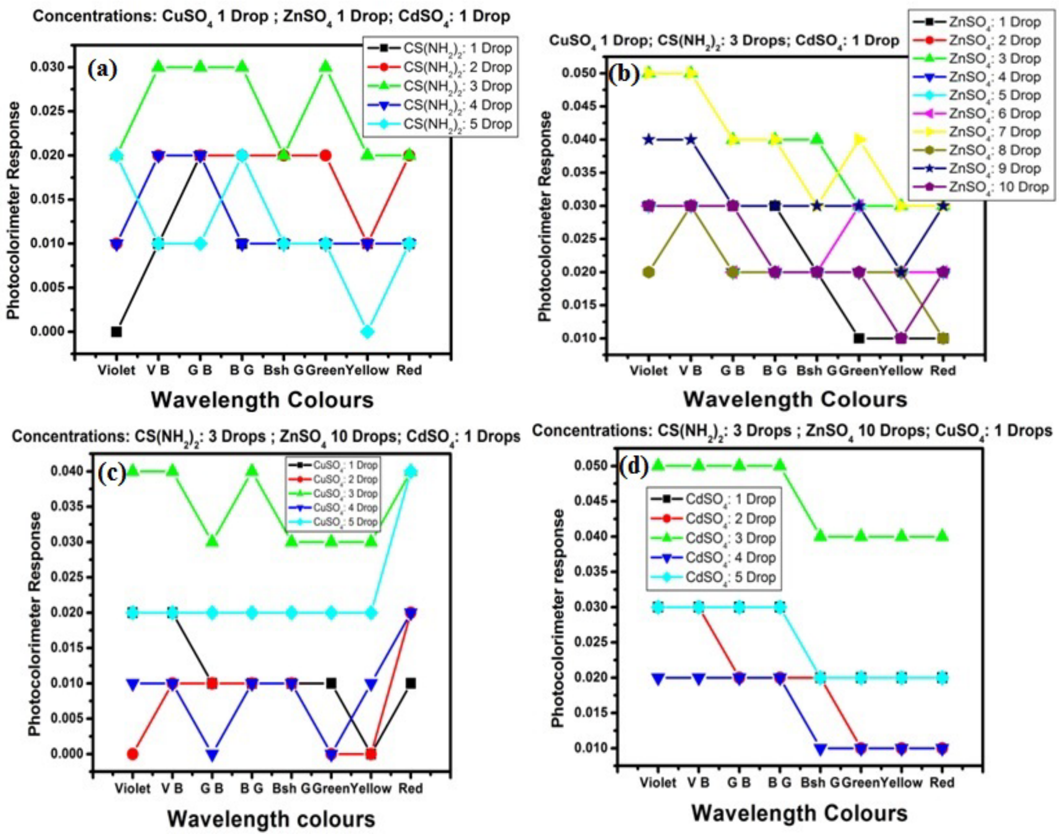

Fig. 4. (a-d) Photo-colorimeter wavelength band responses during Cu_2ZnCdS_4 compound real time formation.

Similarly (fig. 4 c-d) shows the photo-colorimeter wavelength band responses for various $CuSO_4$ and $CdSO_4$ concentrations from 1 drop to 5 drops (all other element compositions fixed) during Cu_2ZnCdS_4 compound formation. During Cu_2ZnCdS_4 compound formation, each $CuSO_4$ and $CdSO_4$ concentrations drop increment shows a new specific photo-colorimeter wavelength band response.

3.5. Real time UV-vcisible transmittance studies

Fig 5 (a-d) UV-Visible spectroscopy studies on Cu_2ZnCdS_4 compound real time formation with respect to various ZnSO4, CdSO4, $CuSO_4$ and $CS(NH_2)_2$ concentrations were examined in the wavelength between 350 nm to 950 nm.

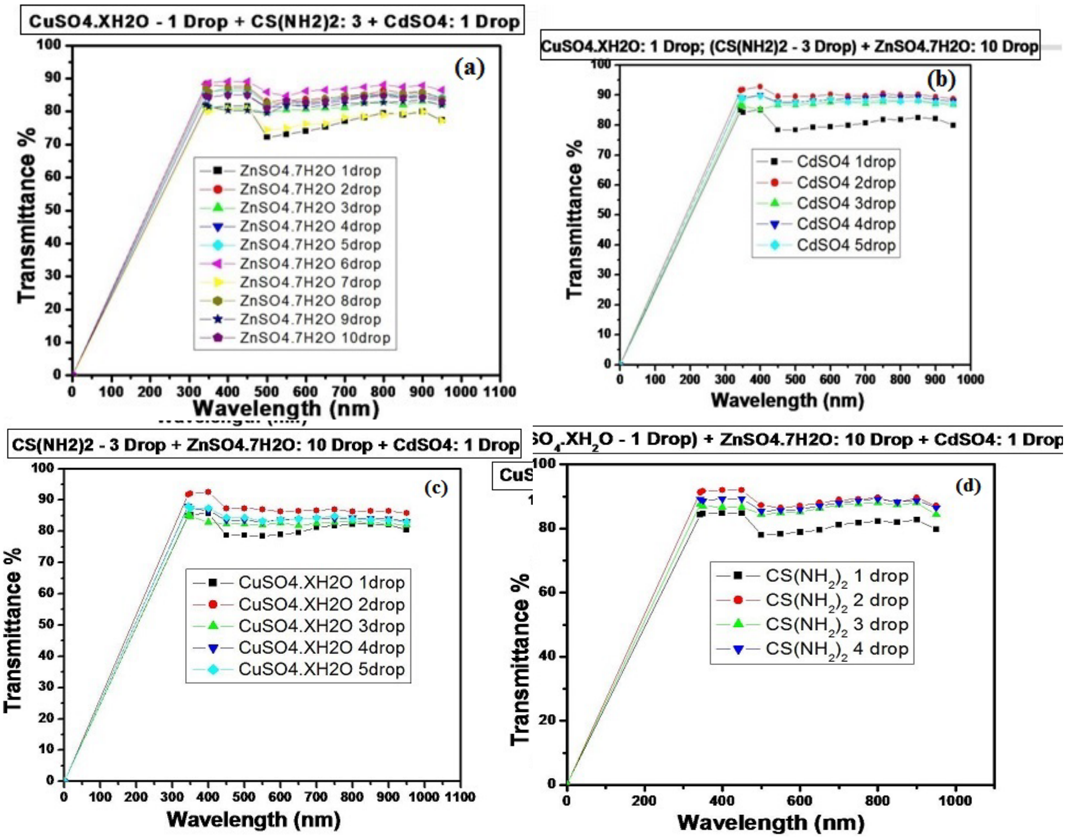

Fig. 5. (a-d) UV-Visible spectroscopy studies on Cu_2ZnCdS_4 compound real time formation.

The real time Cu_2ZnCdS_4 compound formation transmittance results showed the %Transmittance increased when $ZnSO_4$ concentration increase. For all of $ZnSO_4$, $CdSO_4$, $CuSO_4$ and $CS(NH_2)_2$ concentrations the optic %transmittance fall in the range between 80% to 90%. So one can tune the transmittance Cu_2ZnCdS_4 compound from 80% to 90% even few drops $ZnSO_4$, $CdSO_4$, $CuSO_4$ and $CS(NH_2)_2$ concentrations changes and this is most important material compound property for any optics and optoelectronic applications.

3.6. Digital photo fluorometer studies on real time Cu_2ZnCdS_4 compound formation

Digital photo fluorometer studies on Cu_2ZnCdS_4 compounds were investigated with help of two primary filters such as 5840 Å and 5113 Å. Three different secondary filters used for the real time compound formation study. Most of Cu_2ZnCdS_4 compounds real time results showed good fluorescence when using both primary filters 5840 Å and 5113 Å respectively. For all of the measurements the utilized secondary filters are in the specific wavelength range of 4308, 3486 and 3385 Å respectively. Fig 6 shows the photon emission characteristics of real time Cu_2ZnCdS_4 compound formation with respect to various $CdSO_4$ concentrations from 1 drop to 5 drops.

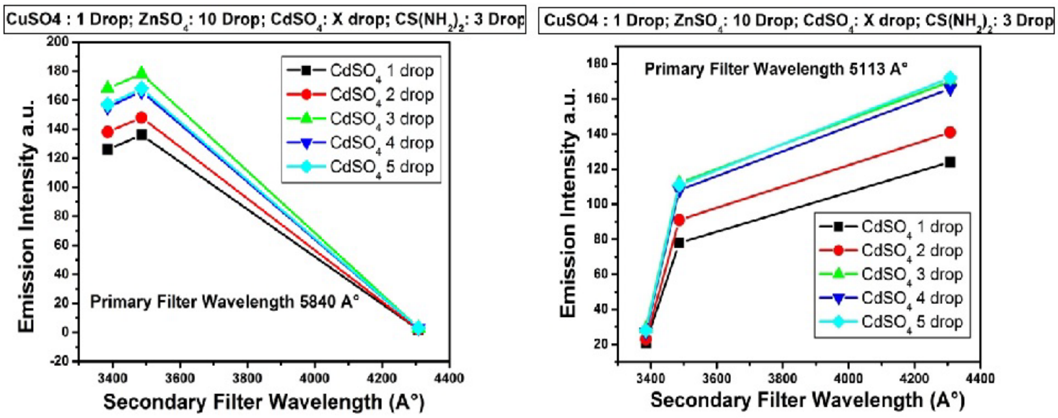

Fig. 6. The photon emission characteristics of real time Cu_2ZnCdS_4 compound formation under two different primary filters, three different secondary filters.

Fig. 7 shows the photon emission characteristics of real time Cu_2ZnCdS_4 compound formation under two different primary filters, three different secondary filters conducted for several hundred samples. In this present research article we present only the $CuSO_4$ and $CdSO_4$ concentration changes from 1 drop to 5 drops due to the very interesting emission changes observed for various $CuSO_4$ concentrations and $CdSO_4$ concentrations than the $CS(NH_2)_2$ and $ZnSO_4$ concentrations change. So that we presented these two element compositions change based emission characteristics. From the present fluorescence results we can understand that the $CuSO_4$ concentration at 2 drops showed high emission than all of other $CuSO_4$ concentrations.

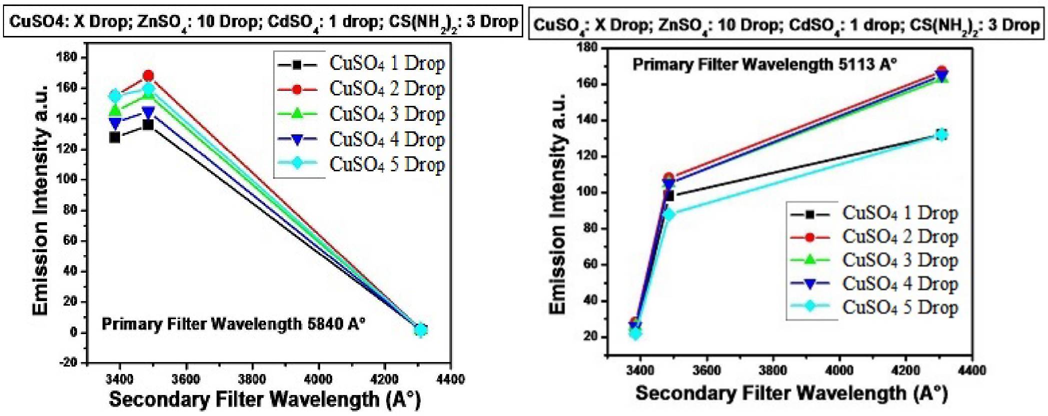

Fig. 7. The photon emission characteristics of real time Cu_2ZnCdS_4 compound formation under two different primary filters, three different secondary filters.

4. Conclusion

In the first step the Cu_2ZnCdS_4 material synthesized with different $CS(NH_2)_2$, $ZnSO_4$, $CuSO_4$ and $CdSO_4$ ions concentration. For all samples the measurements investigated in real time and presented in this research article. The pH, EC, TDS, photocolorimeter, UV-Vis spectroscopy and photo fluorometer studies were successfully investigated on the real time Cu_2ZnCdS_4 quaternary compound formation. The real time pH value studies on Cu_2ZnCdS_4 compound showed the drastic change in pH value. Various $ZnSO_4$, $CuSO_4$, $CdSO_4$ and $CS(NH_2)_2$ ions concentrations showed most sensitive pH value increasing and decreasing trend. Even one drop of these element ions concentrations can completely change the total reaction pH value change. This real time results are most important for worldwide materials science and engineering researchers to understand the micro input to macro effects understanding. The real time Electrical conductivity (EC) change value studies on Cu_2ZnCdS_4 compound showed the increasing EC value trend for various $ZnSO_4$, $CuSO_4$ and $CdSO_4$ ions concentrations and showed decreasing trend for increasing $CS(NH_2)_2$ concentration.

In case of TDS measurement, we found one important fact that the gradual increment of $ZnSO_4$ (1 to 10 drops) and $CuSO_4$ concentration (1 to 5 drops), the TDS meter showed similar increasing trend value. The TDS value also increased for $CdSO_4$ concentration 1 to 2 drops (1450 ppm to 1800 ppm), maintaining steady TDS value when $CdSO_4$ from 2 to 4 drops (1800 ppm) and further increasing to 5 drops leads again TDS value increasing (1850 ppm). In Photo colorimeter measurements especially, we measured the mixed colour wavelengths such as violet-blue, green-blue, blue-green, bluish green followed by monochromatic responses for all the samples respectively. The photo-colorimeter response displayed the most interesting graph theory art like drastic change with respect to increase in $ZnSO_4$, $CuSO_4$, $CdSO_4$ and $CS(NH_2)_2$ ions elemental concentrations

From the UV-Vis spectroscopy studies on real time Cu_2ZnCdS_4 compound formation we concluded that the following. For all of $ZnSO_4$, $CdSO_4$, $CuSO_4$ and $CS(NH_2)_2$ concentrations the optic %transmittance fall in the range between 80% to 90%. Digital photo-fluorometer studies on Cu_2ZnCdS_4 compounds were investigated with help of two primary major filters (5840 Å & 5113 Å) and three different secondary filters (4308, 3486 & 3385 Å). Among several hundred sample photo emission characteristics, various $CuSO_4$ and $CdSO_4$ concentration changes from 1 to 5 drops exhibited very interesting emission changes than the $CS(NH_2)_2$ and $ZnSO_4$ concentrations changes.

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