

Study of the CuS/CdSe Quantum Dots on the Optical Properties of Green Synthesis

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Abstract

Chalcogenides based nanomaterials, such as CdSe are emerging as an important material offering transformative potential across multiple domains, such as photocatalysis, optoelectronics, sensing, and photo luminesce. In this study we synthesised CuS/CdSe quantum dots by varying CuS concentration through plant mediated green method. The copper sulfide synthesized at varying concentrations of the Se source, exhibited bonding configuration that are comparable to those of the Cd source. The goal of this igniting interest in these CdSe based composites, is by highlighting their numerous advantages across diverse applications. The FTIR spectra of these systems, exhibit a prominent vibrational peak at 732 cm^{-1} and a strong vibrational stretching band at 512 cm^{-1} belongs to N-H banding vibration. FTIR spectra in the higher-energy region, reveals an absorption peak, which can be attributed to the O-H stretching. The absorption spectra obtained through UV-visible absorption spectroscopy were recorded in the range of 200-800 nm. Using the Tauc formula, the band gap was calculated and it is 3.52 eV for pure CuS quantum dots and 2.93 eV for CuS/CdSe quantum dots, the method for regulating the light emission wavelength, attributed to the anticipated blue shift in absorption spectra. It is observed that the recorded photoluminescence emission spectra are in the absorption band edge state. The CS2 showed an emission peak at 378 nm, indicating a blue shift, as a result of the interaction between carriers and phonons. The improved photoluminescence properties of these systems will make them suitable for optoelectronics applications.

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INTRODUCTION

Green methods uses eco-friendly materials, those are non-toxic, from renewable sources, such as, different parts of plants, such as stem, leaves, flowers, fruits, etc., bacterial or fungi based methods, and uses biodegradable materials. Where the conventional synthesis uses toxic solvents, hazardous and toxic materials, including heavy metals, toxic solvents, causing great environmental issues and disposal. Plant extracts contain different organic compounds, such as flavonoids, phenolics, alkaloids, polyphenols, etc., and these will act as reducing and stabilizing agents during the synthesis of nanostructures. At the same time, they help in preventing agglomeration. The Cadmium selenium (CdSe) is identified as an *n*-type material with narrow band gap energy of 2.42 eV [1]. The semiconducting properties of CdSe are linked to the

presence of sulfur vacancies, which result from an excess of cadmium atoms. Furthermore, CdSe demonstrates a remarkable capacity for absorbing the visible spectrum of light [2], making it advantageous for applications in the visible range. These interesting characteristics of CdSe make it suitable for numerous applications, such as in optoelectronic technologies [3]. Although CdSe has promising potential, it has a challenge in efficiently separating generated electron–hole pairs. These challenges are due to its limited surface area, suboptimal light manipulation efficiency, and insufficient active sites. The swift recombination of the produced charge carriers is affected by these elements, thereby reducing the quantum efficiency [4]. Several researchers worked for preparing CdSe in the nanoform to improve the separation of electron–hole pairs, Shaikh et al synthesized nano-CdSe with exhibited significant efficiency in the separation of photogenerated electron–hole pairs [5]. On the other hand, a different treatment strategy utilizing CdSe seeks to tackle the challenge of swift recombination of photogenerated charge carriers. Methods to achieve this include nonmetal doping, combining with other semiconducting materials [6], coupling with noble metals [7], or incorporating organic quantum dots. The development of the internal electric field at the interface has garnered considerable attention because of its function in facilitating the separation of induced carriers [8]. This method has the potential to prolong the lifespan of charge carriers, consequently improving the optical properties [9].

The copper sulfide CuS is identified as a *p*-type semiconducting material, demonstrating an energy gap of around 2 eV. The CuS has attracted significant interest due to its exceptional electrical and optical characteristics [10]. CuS exhibits a range of available electron state pairs and vacancies, which may facilitate improvements in the process [11]. As a result, CuS emerges as an intriguing choice for noble metals employed as, owing to the presence of vacant 3*p*-orbitals in the sulfur atom that function as electron acceptors [12]. The heterostructures created between CuS and CdSe system, particularly CuS/CdSe, has demonstrated impact, on overall band gap position of the system. Moreover, they successfully prevent the recombination of photoexcited electrons, thus improving the green synthesis [13].

The CuS/CdSe quantum dots exhibits an adjustable bandgap (tunability) with size and composition variations, which is an important optical property. It was found that the composite formed from CdSe/CuS micro flowers shows exceptional activity under visible light. The composites of CdSe/CuS with different molar ratios, produced via the hydrothermal method, displayed improved optical efficiency for evolution, achieving a rate corresponding to the variation in CdSe/CuS concentration [14]. The CuS/CdSe nanocomposite, synthesized via a wet impregnation method, showed a notable improvement in charge generation and efficiently controlled the recombination of photogenerated electron–hole pair, exceeding the effectiveness of pure CuS, pure CdSe, and various composites formed by mixing CdSe and CuS in alternative ratios [15]. A noted decrease in PL intensity in the CdSe/CuS quantum dots, linked to the separation of electrons and holes. It was shown that altering the chemical composition of mesoporous networks made up of interconnected CuS and CdSe leads to a notable enhancement in photocatalytic activity. Furthermore, the investigation demonstrated that the mesoporous CuS/CdSe containing around CuS attained an average evolution rate with a quantum efficiency (QE) of at a wavelength of 420–510 nm. Likewise, it exhibited impressive stability, exceeding the performance of the pure mesoporous CdSe sample, assessed under the same conditions [16].

This investigation examines the distinctive characteristics that may emerge from alloying of CuS and CdSe in different properties. This study examines the impact of the composition of different concentration on the properties of the synthesized nanocomposites CuS/CdSe quantum dots, produced via green method. Various concentrations of CuS/CdSe QDs have been prepared in large quantities, through green method. All of them demonstrated stability and they are labelled as CS, CS0.5, CS1, CS2. The CuS/CdSe quantum dots exhibit characteristics of direct semiconductor, featuring relatively narrow band gaps of 3.04 and 3.52 eV, along with high absorption coefficient, position them as promising material for absorption applications. This work focus to achieve distinctive optical characteristics, including high photoluminescent quantum yield, and composition-dependent bandgap, a broad emission range, significant Stokes shift, and prolonged photoluminescence. The size and compositions of QDs results in adjustable wavelengths, enabling change in display colours in LEDs.

EXPERIMENTAL TECHNIQUES

Materials

The Copper sulphate (CuSO_4) (AR Grade m.w.: 159.609), Cadmium sulphate [CdSO_4] [AR grade, m.w. 256.50], Sodium sulphate [Na_2SO_4] [AR Grade, m.w. 142.04], Methanol [CH_3OH] AR Grade, Chloroform [CHCl_3], and Deionized water were purchased from SD fine Chemicals Ltd., India. Selenium powder [Se] [m.w. 78.96] was purchased from Sigma-Aldrich Pvt. Ltd. Fresh *Moringa oleifera* leaves were plucked from local gardens in Hyderabad.

Preparation of Plant Extract

Fresh *Moringa oleifera* (MO) leaves were collected from the Osmania University campus garden, Hyderabad, Telangana. To remove impurities, the leaves were thoroughly washed three times with distilled water and dried in shade for 5 hours. Then these leaves were finely ground using a micro-grinding machine. A 20 g sample of ground leaves was mixed with 100 mL of methanol and then the mixture was incubated with agitation at 70°C for 95 minutes, then filtered using Whatman No. 1 paper, yielding a clear plant extract for further use.

Preparation of CuS/CdSe Quantum Dots

To synthesize CuS/CdSe quantum dots, a solution of 0.25 M CuSO_4 in 5 mL of distilled water was prepared and stirred for 20 minutes. This solution served as the precursor for subsequent synthesis steps. Different concentrations of 0.28 M, 0.57 M, and 1.28 M solutions were prepared and utilized for various experiments.

Take a 1:1 molar ratio of 10 mL of 0.28 M CdSO_4 and 0.57 M selenium [Se] powder and dissolved in 15 mL of distilled water, stirred for 40 minutes to produce a clear solution. This will be used as a precursor in the synthesis of CdSe nanoparticles. In the first phase, 15 mL of 0.28 M CuSO_4 was prepared and combined with 15 mL of CdSe solution [at concentrations of 0.28 M and 0.57 M] and 20 mL of *Moringa oleifera* leaf extract. In the second phase, 15 mL of 0.14 M Na_2SO_4 was added to the mixture and incubated for 5 days at 70°C . The resulting solution was centrifuged to isolate quantum dots. The quantum dots were dried in a hot air oven at 90°C for 3 hours, producing a dry solid pellet for further studies. The entire process is shown in Figure 1.

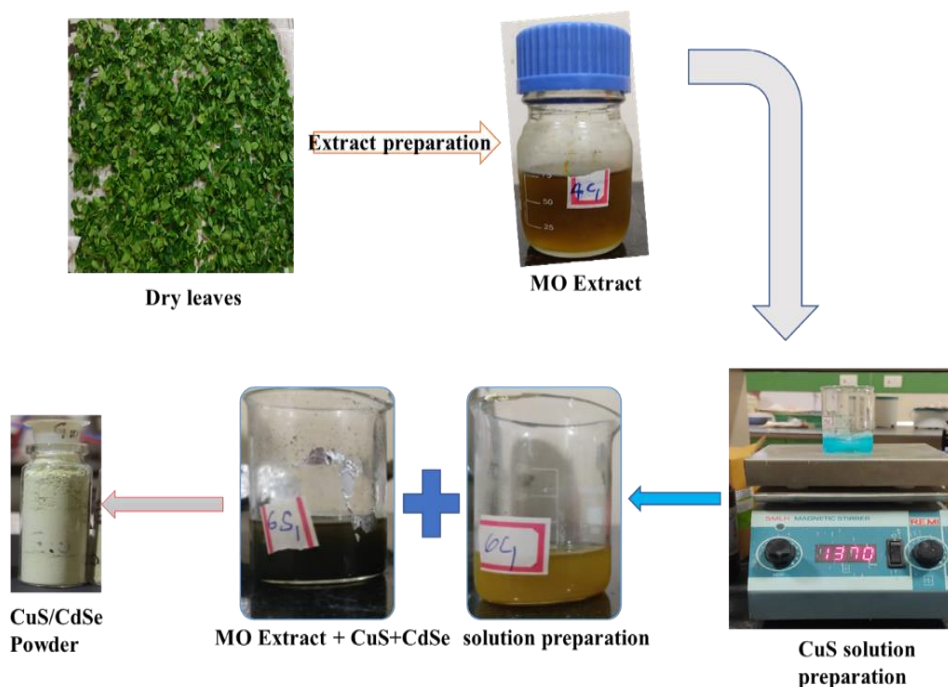


Figure 1. Process of preparing the CuS/CdSe quantum dots by green method.

Material Characterization Techniques

The UV-vis spectra was obtained with SHIMADZU-1800 UV-vis spectrophotometer in the wavelength of 200–1000 nm. The Fourier-transforms infrared spectrometers (FTIR) was recorded at room temperature, in transmittance mode to identify the functional groups, operating in the range of 400–4000 cm^{-1} . The Shimadzu RF-5301 Spectrofluorophotometer was used to record the photoluminescence (PL) emission spectrum.

RESULTS AND DISCUSSION

FTIR analysis of CuS/CdSe

The FTIR analysis of CuS/CdSe quantum dots exhibit a various of functional groups and chemical bonds. The FTIR spectra of CdS/CdSe loaded with varying concentrations of CuS of are presented in figure 2. The stretching vibrations of C-H bonds seen in the sample's surfactants are indicated by 774 cm^{-1} [17]. The vibrational band observed at 625 cm^{-1} corresponds to the symmetric bending of the water molecule. The sample synthesized at varying sulfur concentrations exhibits a prominent vibrational peak at 732 cm^{-1} , is associated with the carbonyl group (C-O).

The bending vibrations of H-O-H bonds in water molecules are linked to 1150 cm^{-1} [18] and 1208 cm^{-1} the bending vibrations of O-H bonds, which are important for functional groups that might interact with CuS/CdSe quantum dots, are represented by the measured. 1061 cm^{-1} . This shows how C-O bonds stretch, which may indicate that sulfur functionalities were used in the creation of these semiconductor composites. Vibrations linked to inorganic bonds, the lattice vibrations of the Cu-S, are shown by 627 cm^{-1} [19]. The bending vibrations of Cd-S bonds in semiconductor materials are linked to 527 cm^{-1} the relationship between CuS and CdSe at the molecular level. The Table 1 shows the peak positions for various vibration modes. The interactions affect the composite's electrical or optical characteristics.

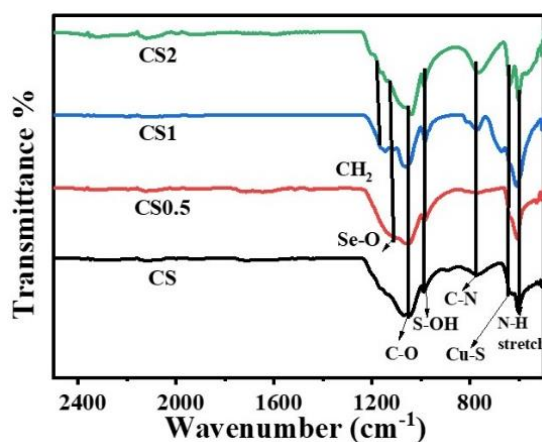


Figure 2. FTIR spectra of CuS/CdSe quantum dots.

Table 1. FTIR peak positions of CuS/CdSe quantum dots.

Vibrational Modes	CuS	CS0.5	CS1	CS2
N-H stretching vibration	604	605	606	599
Cu-S stretching vibration	627	635	672	635
O-C-N stretching vibration	774	777	774	762
C-C stretching vibration	873	-	822	-
S-OH stretching vibration	987	983	985	986
Cu-OH stretching	-	-	-	1038
C-O Stretching vibration	1061	1058	1058	1066
Se-O stretching vibration	1137	1107	1150	1175
CH2 asymmetric Stretching vibrations	-	-	-	1208

Photoluminescence of CuS/CdSe

The Figure 3 illustrates the photoluminescence emission spectra of the CdS/CdSe quantum dots and table 2 summarizes E_m value. The emission of the sample CS varies peak position 371 nm. The CuS/CdSe quantum dots of CS2 high emission peak intensity of sample 378 nm of pure CuS and CdS/CdSe quantum dots [20]. The emission peaks observed in photoluminescence spectra are noted at CS shorter wavelengths in comparison to the indication peak. The sample in its factors are suggested as influencing the characteristics of the observed spectra of CS. The interaction between carriers and phonons in quantum dots has been observed to exhibit a peak shift in the photoluminescence emission spectra concerning the absorption band [21]. The emission of blue-shift increased peak from the interaction between carriers and phonons, where photo-excited carriers on interact with phonons with higher excited energy states. The interaction between carriers and phonons results in peak broadening and creates a dependent asymmetry that favors higher energies in the photoluminescence [22]. The PL spectra observed in the CuS/CdSe system is suggested to be the bandgap resulting from quantum confinement. The precursor of the CS2 sample comprises the Cd^{+} cations radius of the CdSe intermediate complexes. The noted blue shift, low wavelength asymmetry, and broadening of the PL peak result from the presence of intermediate complexes that function as zero-dimensional clusters, and quantum confinement effects. The pronounced intensity of PL peaks suggests that radiative recombination in the CuS/CdSe quantum dots synthesized in this study is minimal, indicating that the material exhibits a good confinement effect.

UV-Visible of CuS/CdSe

The UV-visible absorption spectra of the CuS/CdSe quantum dots were obtained using the Rayleigh UV-2601 spectrometer. The optical studies were performed across the wavelength range of 200 – 800 nm, as depicted as Figure 4. Nonetheless, unique absorption peaks appeared in 300 to 400 nm range, and the location of these peaks, as depicted in Table 3, suggested the band gap of the quantum dots [23, 24]. The UV-visible spectra demonstrated a blue shift in the absorption band relative to the CS material.

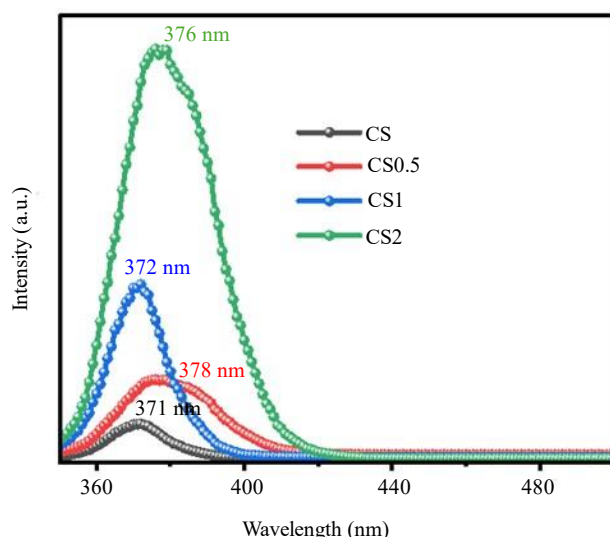


Figure 3. Photoluminescence spectra of CuS/CdSe based samples.

Table 2. Photoluminescence λ Max of CuS/CdSe Samples.

S.N.	Sample	Em λ (max)
1	CS	371
2	CS0.5	378
3	CS1	372
4	CS2	376

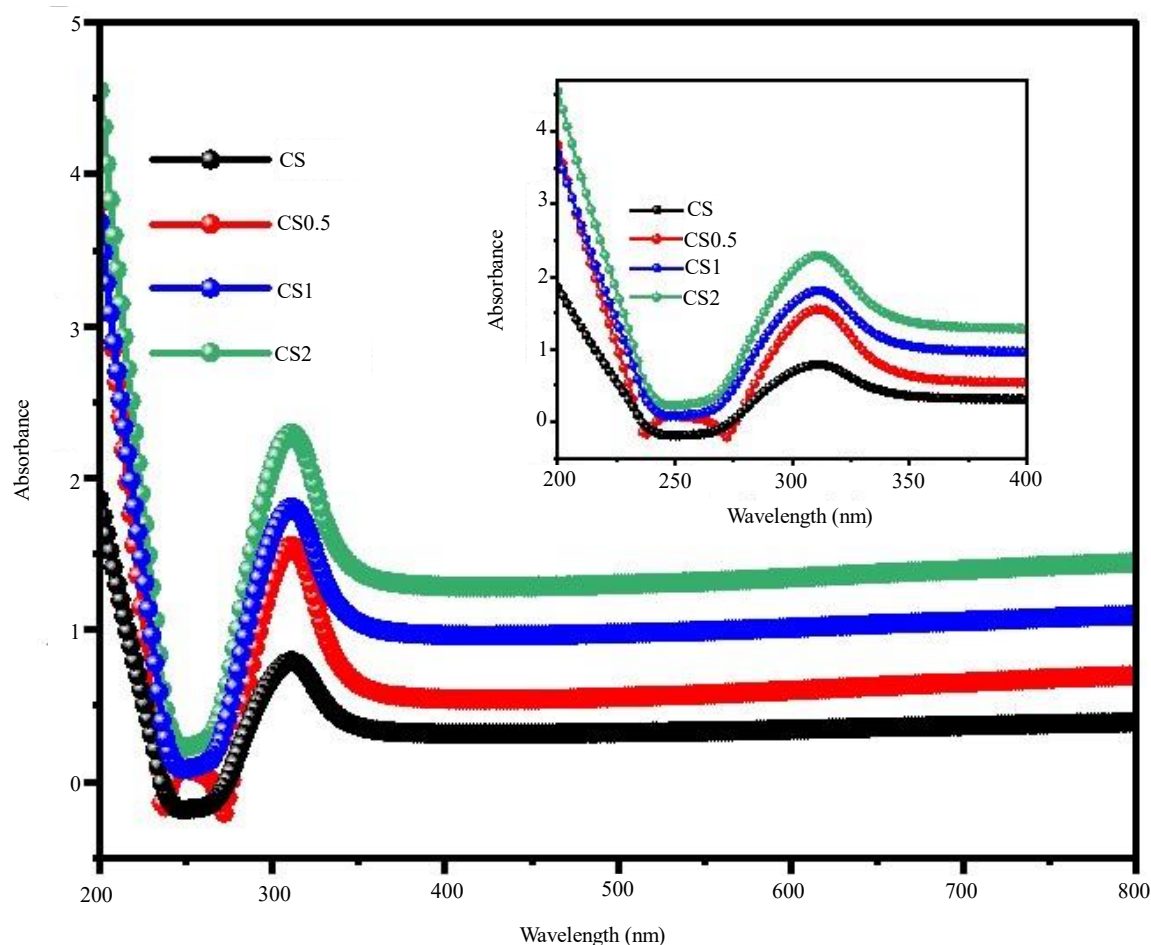


Figure 4. UV-visible spectra of CS, CS0.5, CS1, and CS2.

Table 3. Peak positions of UV-visible absorbance spectra of the samples.

S.N.	Sample	Wavelength [nm]	Absorbance
1	CS	308	2.98
2	CS0.5	310	2.76
3	CS1	312	3.89
4	CS2	315	4.54

Band Gap Energy Calculations

The fundamental band edge reveals that both indirect and direct transitions take place in the photon energy absorbing material. The band energy associated with these transitions can be ascertained by plotting $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$). The energy bandgap of the CuS/CdSe quantum dots was established by graphing $(\alpha h\nu)^2$ versus $h\nu$ and extending the linear portion of the curve to the energy of a photon. The optical band gap was determined from absorption spectra using the Tauc equation [25].

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

In this context, α indicates the absorption coefficient, A stands for a constant, and E_g refers to the direct band gap energy of the material. The values of m are $1/2$, 2 , 3 , and $3/2$ corresponding to direct band gap transitions respectively. The existing follows the principle of direct band gap transition (i.e., $m = 1/2$). The band gap energy for the quantum dots CS and CS2 samples was found to be 3.52 eV and 2.93 eV respectively, as shown in Table 4, along with other values.

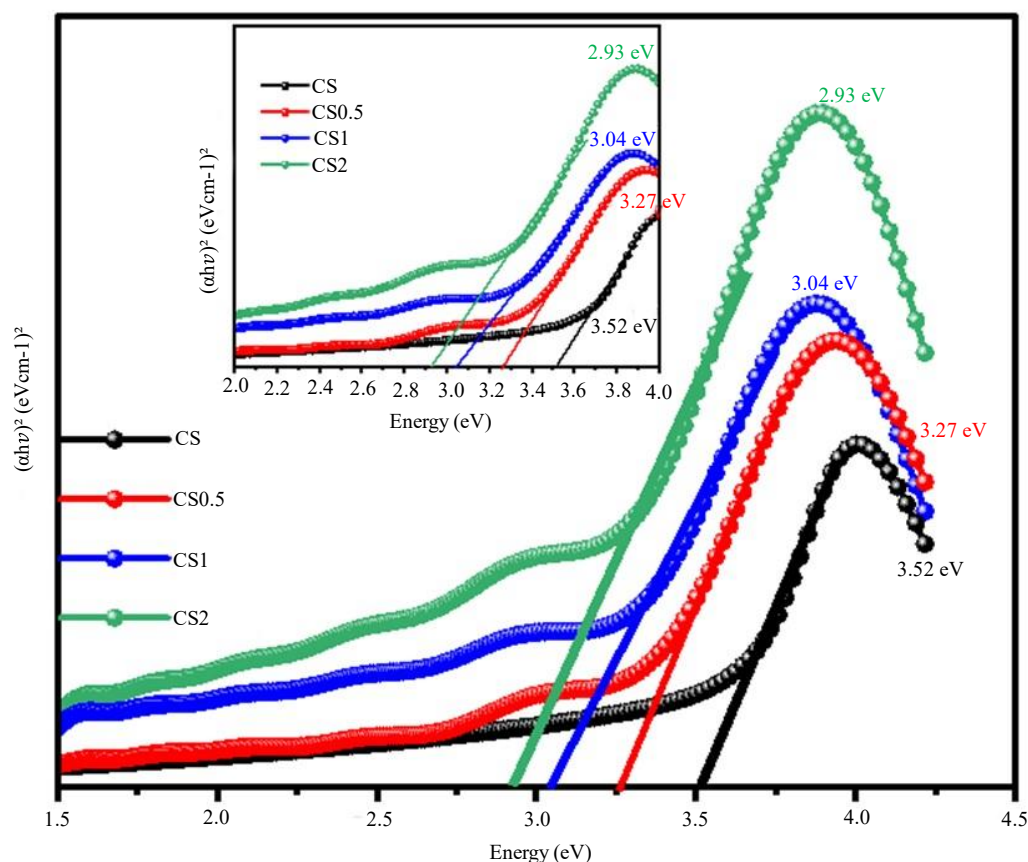


Figure 5. Direct bandgap energy of the prepared samples.

Table 4. Bandgap energy derived from tauc plots of CS, CS0.5, CS1, CS2.

S.N.	Samples	Eg [eV]
1	CS	3.52
2	CS0.5	3.27
3	CS1	3.04
4	CS2	2.93

The results demonstrate that the energy band gap decreases with the incorporation of CuS in CdS/CdSe system [25, 26]. This result may be linked to the change in the materials dimension after the CuS contents. The Figures 5 present the absorption spectra and energy band gap of samples under study.

CONCLUSION

The CuS/CdSe QDs were synthesized through a green synthesis process utilizing. The impact of varying concentrations of CuS. The Se exhibits bonding formations that are comparable to those of the Cd. The FTIR identification of the C-O and N-H peaks corresponding to 604 cm^{-1} and, 873 cm^{-1} . The dimensions of the CuS/CdSe QDs in the Results optical band gap energy values were approximately 3.52 eV. The increase in the CS concentration and CS2 reduction of the band gap value 2.93 eV. The photoluminescence is the emission of the sample CS peak position 371 nm. The CuS/CdSe quantum dots of various sample CS2 high emission peak intensity of sample 378 nm of pure CuS and CdS/CdSe quantum dots. The blue and green emissions support the presence of copper and sulfur vacancies. The intense blue emission from these materials suggests their potential application. The CS various optical performance compared to all changed concentrations. The improved performance of the CS2 sample decreases in band gap energy. Therefore, this concentration varies in light absorption and can serve as a quantum dot.

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