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Optical and Electrical Properties of CDSE Core/Shell Nanocrystals Dispersed In Polyvinyl Alcohol for Optoelectronic Devices

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ABSTRACT

Research on CdSe core/shell Nano crystals dispersed in PVA has attracted a lot of interest because of the optoelectronic devices that might benefit greatly from their exceptional electrical and optical characteristics. Because of quantum confinement phenomena, CdSe Nano crystals have variable bandgaps, high absorption coefficients, and size-dependent emission. But they aren't very effective due to surface trap states and unpredictable environments. Surface flaws are successfully passivated, photoluminescence efficiency is enhanced, and chemical and thermal stability are improved by introducing a core/shell structure. To further avoid aggregation, offer environmental protection, and assure uniform film formation suited for device construction; these nanocrystals may be embedded into a transparent and flexible polymer host, such PVA. In the end, the hybrid Nano composites have adjustable electrical characteristics, improved luminescence stability, and programmable absorption and emission in the visible spectrum. This makes them very adaptable for use in LEDs, solar cells, and photo detectors. Further, PVA's cost-effectiveness, processability, and scalability make it an ideal host matrix for large-area and flexible device integration. By demonstrating the versatility of CdSe-PVA Nano composites as a platform for multifunctional materials, this study bridges the gap between theoretical investigations of nanomaterials and their technical implementation in next-generation optoelectronics.

Keywords: Core/Shell Structure, Polyvinyl Alcohol, Quantum Confinement, Photoluminescence, Optoelectronic Devices.

INTRODUCTION

Because of their exceptional size-tunable electrical and optical characteristics, semiconductor nanocrystals—also called quantum dots—have become a groundbreaking class of materials. Of them, cadmium selenide (CdSe) nanocrystals stand out due to their well characterized luminescence properties, high absorption coefficients, and clearly defined quantum confinement effects. When created as CdSe core/shell nanocrystals, these materials outperform bare CdSe cores in terms of surface passivation, photoluminescence efficiency, and stability. Nanostructures like this hold great promise as next-gen photodetectors, solar cells, and light-emitting diodes (LEDs) due to their tunable emission wavelengths, which may be achieved by adjusting the core size and shell thickness. Materials for optoelectronic devices must be stable under operating circumstances, have excellent charge transfer capabilities, and harvest light efficiently. Surface trap states and non-radiative recombination pathways diminish the optical efficiency of bare CdSe nanocrystals. To improve confinement efficiency, decrease Auger recombination, and passivate surface dangling bonds, a shell material is often used, usually composed of ZnS or CdS. Because of their core/shell configuration, CdSe nanocrystals have greater quantum yields and adjustable emission spectra, which make them ideal for use in devices. Their excellent color purity and small emission linewidth are also important properties for lighting and display technology. [1]

The processability of CdSe core/shell nanocrystals is an important aspect that must be considered when integrating them into devices. Uniform dispersion, improved mechanical stability, film-forming capabilities, and environmental endurance are all benefits of embedding them in polymer matrices. Polyvinyl alcohol (PVA) is one of the most popular polymers because of its many useful qualities, including its high chemical resistance, capacity to host nanocrystals without altering their fundamental characteristics, and high optical transparency. For the development of affordable, scalable optoelectronic components, PVA's compatibility with flexible substrates, water solubility, and excellent film-forming capacity are crucial. The combination of PVA and CdSe core/shell nanocrystals has created new possibilities for the fabrication of hybrid nanocomposites, which can have their electrical and optical characteristics adjusted. It is possible to modify these composites such that they exhibit better charge transport kinetics, photoluminescence stability,

and regulated visible range absorption. Optoelectronic devices that depend on efficient photon-to-electron or electron-to-photon conversion processes absolutely need these features. In addition, nanocrystals added to PVA reduce photobleaching, prevent aggregation, and make sure that large-area films emit the same light. The optical characteristics of CdSe nanocrystals may be better understood by focusing on the idea of quantum confinement. The formation of discrete energy levels and the size dependence of the bandgap occur as the particle size approaches the exciton Bohr radius. By manipulating the nanocrystal's size, one may get exact control over the absorption and emission wavelengths. [2]

For example, the blue-green emission area is emitted by smaller CdSe cores while the red emission region is emitted by bigger ones. A shell further limits nonradioactive decay routes and affects exciton confinement. Therefore, unlike bulk materials, CdSe core/shell nanocrystals provide spectrum tunability in addition to excellent efficiency. These composites are only suitable for use in devices with certain electrical characteristics, such as conductivity, charge mobility, and dielectric response, in addition to their optical performance. The electrical behaviours is changed when nanocrystals are embedded in PVA because localized states are introduced and dielectric environments are adjusted. Nanocrystal concentration and surface functionalization control PVA's conductivity, which makes it amenable to insulating and semiconducting applications in device designs. For instance, light-emitting diodes (LEDs) have minimal energy losses thanks to their modest electrical conductivity and excellent photoluminescence efficiency. On the other hand, improving solar devices' efficiency requires fine-tuning their charge separation and transport mechanisms. It is also important to consider how stable CdSe core/shell nanocrystals will be. Heat, oxygen, and moisture may all weaken luminescence and structural integrity. But gadgets have a longer operating lifespan after being encapsulated in PVA, which greatly enhances their resilience to external factors. In addition, functional groups may be readily introduced to PVA by chemical modification, which improves device performance by increasing nanocrystal dispersion and contact with external electrodes. [3]

The adaptability of CdSe-PVA Nano composites has been shown via research in several optoelectronic applications. These composites provide stable, high-brightness emission colours that may be adjusted for use in displays. They improve the absorption of light and allow for the passage of charges across active layers in solar cells. Because they are so good at producing and dissociating exactions, these materials have excellent sensitivity and response times when used as photo detectors. Dispersed CdSe core/shell nanocrystals in PVA have vast technological potential, as shown by their multifunctional properties. A strong and flexible material platform for optoelectronic advancements is CdSe core/shell nanocrystals embedded in polyvinyl alcohol. Compatible with contemporary device manufacturing methodologies, they provide optical tunability driven by quantum confinement, better stability via core/shell design, and greater process ability using PVA matrices. If we want to build devices that are efficient, stable, and scalable, we need to optimize the relationship between nanostructure design, the polymer environment, and optoelectronic performance.[4]

LITERATURE REVIEW

Doudou, Bessem. (2019) A solution casting approach was used to produce films based on nanocomposites of polyvinyl alcohol (PVA) and multi-walled carbon nanotubes (MWCNT) in varying weight ratios (0 wt%, 1 wt%, 3 wt%, 4 wt%, and 5 wt%). The interaction between the MWCNT and PVA molecule chains was verified by FTIR studies. We estimated the band gaps of PVA/MWCNT nanocomposites using data from a UV-Visible spectroscopy investigation, and we found that the band gaps decreased linearly with the addition of MWCNT. Research using photoluminescence spectroscopy (PL spectroscopy) revealed that, as the concentration of MWCNTs increases, the PVA emission falls into a narrow band at around 400 nm. With a percolation threshold of around 4 wt%, the investigation of I-V characteristics reveals a significant current rise upon MWCNT addition. In addition, they have shown an ideality factor close to 1 when correctly simulated using the existing theory. Potentially useful in future nanotechnology-based systems, these nanocomposites are worth further investigation.

Gadalla, A.et al., (2019) an efficient approach for fabricating quantum dot composites from CdSe (core) and CdS (shell) is attempted to be described in this study. The modified organometallic precursors were used to produce this nanoparticle composite. By comparing X-ray diffraction data with optical spectra and high resolution electron microscopy (HRTEM), we were able to determine the sizes of the nanoparticles using the Debye-Scherer formula. The almost spherical form of the CdSe/CdS NPs reveals that the CdS shell, which is about 0.6 nm thick, completely encases the CdSe core, resulting in a stronger contrast. After the CdS was deposited, UV-Vis spectroscopy revealed a consistent red shift in the absorption and emission spectra, confirming that the shell had grown around the CdSe core. Because the core and shell of a CdSe/CdS structure have identical electron affinities, the holes in the structure are contained inside the core, while the electrons are dispersed across the shell. The thickness of the shell grew due to the prolonged manufacturing process. Results from experiments on produced CdSe/CdS QDs show that the nanocomposite may be used in photonics and optoelectronics.

Kryshtab, Tetyana et al., (2016) The findings from the study on the photostability of composites containing CdSe and Ag-In-S nanocrystals (NCs) embedded in PVA films are published here. Image analysis techniques such as X-ray

diffraction, optical absorption, micro-Raman, and photoluminescence (PL) were used to examine the films. Heating the films to 100 °C enhances PVA crystallization and triggers a rise in PL intensity for both kinds of NCs. The enhancement of NC surface passivation by functional groups of PVA is mostly responsible for the latter result. The films are darkened and the PL intensity is increased for CdSe NCs and decreased for Ag-In-S NCs when the 409-nm LED light is used. As time passes, the Ag-In-S-PVA film's color returns, but the CdSe-PVA composite's altered optical characteristics cannot be unseen. Discussion is centered on the potential processes that lead to the observed effects, including structural changes at the NC/PVA interface and the emergence of novel light-absorbing species.

Sharma, Mamta & Tripathi, S.K.. (2015) The generation of cadmium sulfide nanoparticles in a PVA matrix is accomplished using an in-situ approach. The films are examined using a variety of imaging and spectroscopic techniques, including X-ray diffraction, transmission electron microscopy, photoluminescence, ultraviolet-visible absorption, and Fourier transform infrared spectroscopy. The conduction mechanism is determined by measuring the temperature dependence of the dark conductivity on films of as-deposited PVA:n-CdS nanocomposites. A single activation energy is required for the conduction process in the PVA:n-CdS nanocomposites films. We measure the intensity of steady-state and transient photoconductivity across a wide range of temperatures. The results demonstrate that CdS doped with PVA is an excellent material for solar panels.

Phukan, Pallabi & Saikia, Dulen. (2013) The quantum dot regime consists of CdSe quantum dots (QDs) distributed in a polyvinyl alcohol (PVA) matrix. These QDs were produced using a straightforward heat induced thermolysis method. Using UV-Vis absorption spectroscopy, we examined how different cadmium source concentrations affected the optical characteristics of CdSe/PVA thin films. Through the use of X-ray diffraction (XRD) and transmission electron microscopy (TEM), morphological research, structural analysis, and particle size measurement were conducted on the CdSe/PVA nanocomposite thin films. A hexagonal (wurtzite) structure is shown by the XRD examination of the CdSe/PVA nanocomposite thin film. We produced a CdSe/CdTe thin film solar cell prototype and evaluated its photovoltaic characteristics.

Datta, Anuja et al., (2007) Our three-step procedure for synthesizing CdS/ZnS core/shell nanorods began with solvothermal fabrication of CdS nanorods. Then, we functionalized the CdS surface using a soft chemical process, and last, we grew the ZnS shell. For the purpose of growing a homogeneous ZnS shell covering the surface of the nanorod, citric acid was used as the surface functionalizing agent. When a sulfur source was added, the negatively charged surfaces of the CdS nanorods were aided in the formation of a uniform ZnS shell by the citric acid carboxyl groups that had been trapped there with the -OH functional groups oriented outward. This allowed the Zn2+ ions to attach to the nanorods. Transmission electron microscopy, energy dispersive X-ray analysis, and X-ray studies all corroborated the core/shell nanostructure. Because the ZnS shell effectively passivated the surface electronic states of the CdS cores, the electrical responsiveness and photoluminescence efficiency of the CdS/ZnS core/shell nanorods were much improved compared to the uncoated CdS nanorods. Innovative core/shell nanomaterials with promising uses in optoelectronic devices may be rationally designed with the help of the current synthesis.

EXPERIMENTAL

The sample was mounted on glass slides. Cleaning the glass substrate is crucial. Slides made of commercially available glass that were originally 75 mm x 25 mm x 2 mm were subsequently chopped into 25 mm × 25 mm x 2 mm pieces. After rinsing with deionized water, the glass substrate was cleaned with acetone and methanol in an ultrasonic bath. After the final rinse with nitrogen gas, the glass substrates were completely dry. For the cadmium (Cd) precursor, we utilized cadmium chloride (CdCI), and for the selenium (Se) precursor, we used selenium powder. [5]

A sodium selenosulfite precursor was prepared by heating 8.0 g of Se powder with a 0.5 M sodium sulfite aqueous solution at 70oC for 24 hours while stirring with a magnetic stirrer. After that, the quantity of unreacted Se powder was removed from the reactant using filtering. [6] In order to get a stable, transparent solution, ammonium hydroxide was added to the mixture of Se precursors and the 0.2 M cadmium chloride (CdCI) precursor. We used the spray-atomization technique to get the sample ready.[7] Gases such as nitrogen were used to propel the CdSe solution into the nozzle. Nozzle size was kept constant; however time was employed as the variable parameter in this study, ranging from 10 to 50 minutes.[8] The optical and electrical characteristics have been assessed via the use of photoluminescence spectroscopy (PL) and the I-V characteristic. The experiment was conducted at ambient temperature. [9]

RESULT AND DISCUSSION

The IV characteristic and other electrical parameters were tested at room temperature. Using a conventional two-probe technique, the rectangular samples had a typical area of 2 mm2. [10] Figure 1 displays the current-voltage profile of CdSe nanoparticles on a glass surface. We used the Au metal contact. The electrical profile measuring of materials is a common use of this approach. [11] All measurements were taken with a single sunbeam (AM 1.5, 100mWcm-2). Using the open circuit voltage (Voc), the I-V curve showed that the CdSe nanoparticles were of the n-type.[12]

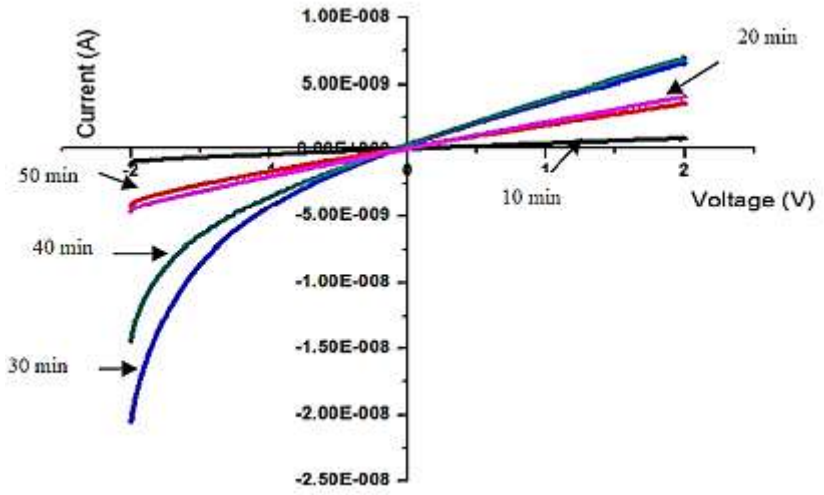


Figure 1: I–V Curve of CdSe Nanoparticles Coated on Glass Substrate

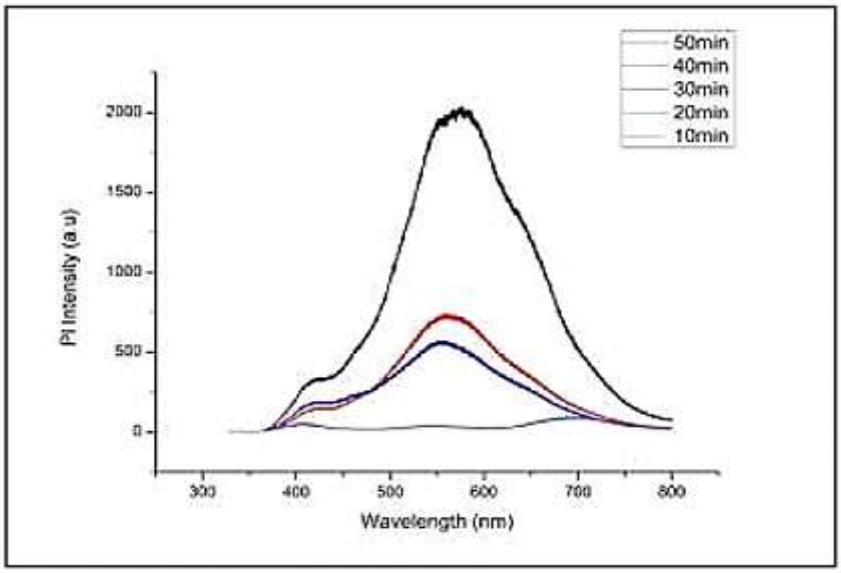


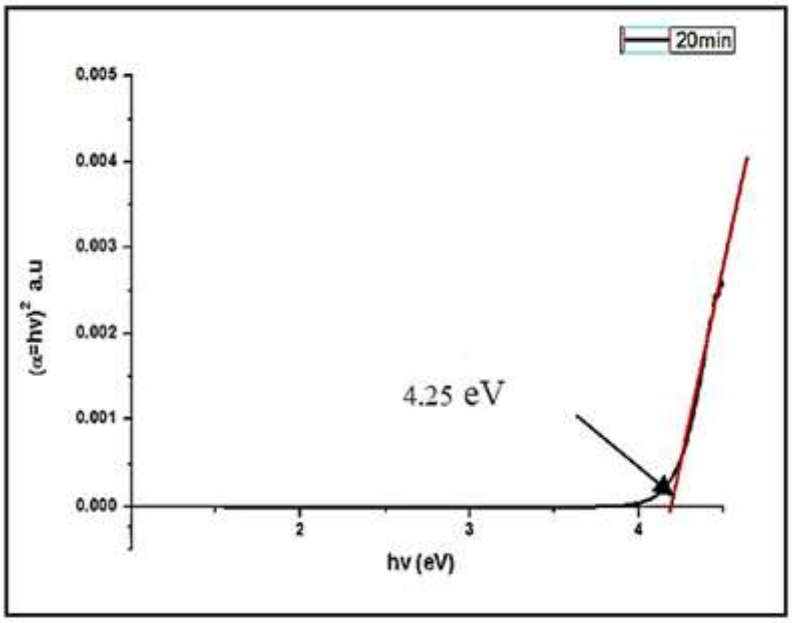
Figure 2: Photoluminescence Response of Spray-Atomized CdSe Nanoparticles on Glass Substrate

A room temperature PL spectrum of CdSe nanoparticles is seen in Fig. 2. Two bands, spanning 400 and 550 nm, are shown in Figure 2.[13] At around 550 nm, the glass substrate exhibited its first peak, which corresponded to CdSe nanoparticles. The optical characteristics of CdSe nanoparticles were investigated in this publication using photoluminescence spectroscopy (PL) from 10 minutes to 50 minutes. At room temperature, the readings were taken. The experimental data reveals that for each band, there are distinct intensities and bands seen at various wavelengths. [14]

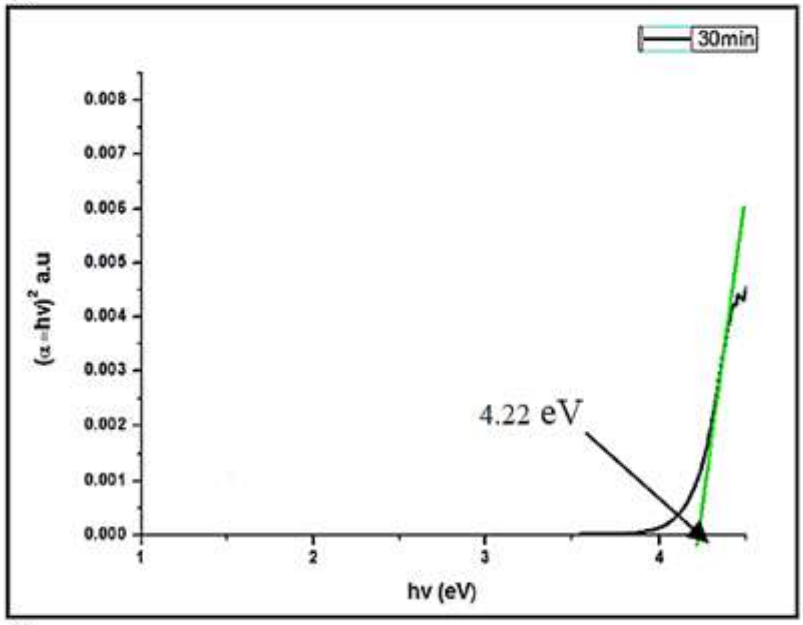
The intensity of PL grows in tandem with the response time, and the peak moves to the right as a result. [15] A shift from blue to red occurs in the spectrum as a result of an increase in wavelength, which occurs when the peak moves from left to right. Particle size is directly proportional to their wavelength, as is well-established in the literature.[16] Figure 2 shows that due to size differences, CdSe nanoparticles exhibit distinct quantum confinement effects. After 10 minutes of laser illumination at 520 W/cm2, this PL spectrum was observed.[17]

Table 1: Size Estimation of CdSe Nanoparticles from PL Spectra

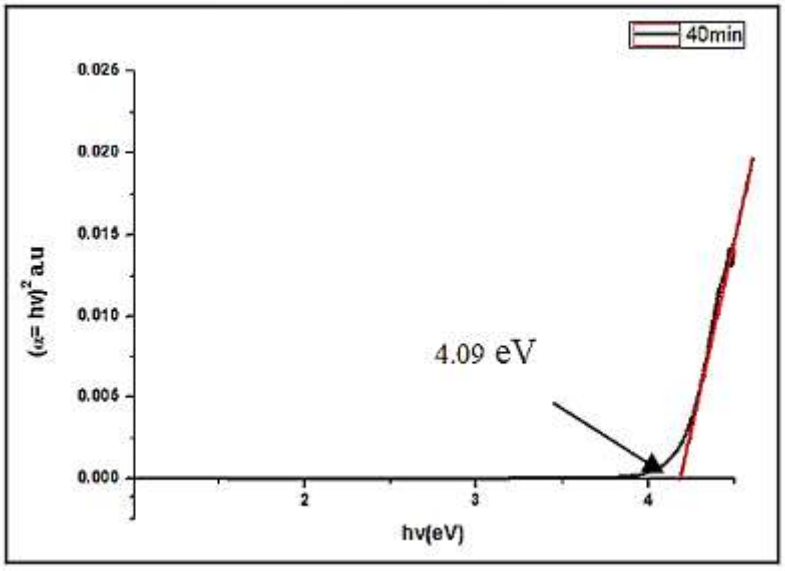
Sample	1	2	3	4	5
Reaction time (min)	10	20	30	40	50
Peak Location (nm)	-	-	553.20	560.85	578.28
Radius (nm)	64.57	46.61	31.61	34.83	35.41
Energy Band Gap (eV)	-	4.25	4.22	4.09	4.21


20min
0.005
0.004
0.003
0.002
0.001
0.000
(α=hν)² a.u
4.25 eV
2
3
4
hv (eV)

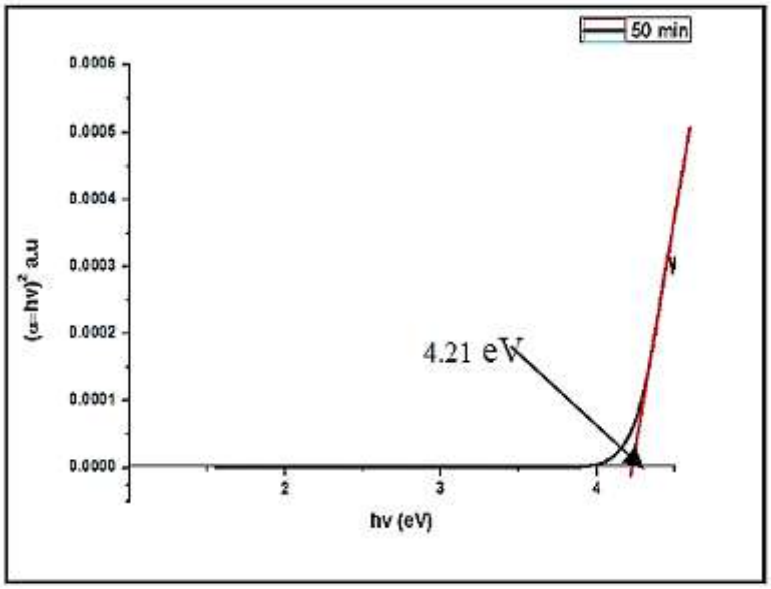
(a)


30min
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
(α=hν)² a.u
4.22 eV
1
2
3
4
hv (eV)

(b)


40min
0.026
0.020
0.015
0.010
0.005
0.000
(α= hν)² a.u
4.09 eV
2
3
4
hv(eV)

(c)



(d)

Figure 3: Variation of Optical Band Gap with Deposition Time Shown by Tauc Plots: (a) 20 min, (b) 30 min, (c) 40 min, (d) 50 min

Figure 3 shows the results of using the Tauc plot to determine the direct energy band gap of CdSe nanoparticles.[18] The band gap of the CdSe nanoparticles, as determined by earlier studies, was around 1.78 eV. The energy band gap was determined using the Tauc plot approach based on Table 1. Over time, CdSe nanoparticles maintained a nearly constant average energy band gap. This research establishes a relationship between particle size and the energy band gap, showing that the latter decreases as particle size increases. [19] The principle of confinement is relevant here. In the area of strong absorption, the values of the absorption coefficient (α) are determined from the transmission data as the basic absorption edge, according to the relation:

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \quad (1)$$

The fluctuation of α with photon energy (hv) is seen in the inset of Figure 3. To find the material's band gap,[20] one uses the fundamental absorption, which is associated with the change from the valence band to the conduction band. We have absorption coefficient α values that are more than or equal to 104 cm^{-1}.[21] A representation of the power law behavior of Tauc may be given by the relation between α and the incident photon energy (hv):

$$\alpha = \frac{A\left(h\nu - E_g\right)^n}{h\nu} \quad (2)$$

The kind of transition determines the exponent η, whereas A is a constant and Eg is the material's optical band gap.[22] The values of η may be 1/2, 2, 3/2, and 3, respectively, which correspond to the permissible direct, indirect, and banned direct and indirect transitions. [23] Images (a), (b), (c), and (d) in Figure 3 demonstrate that the energy band gap was determined using the Tauc plot. The Eg value for CdSe nanoparticles was determined by extending the straight line segment of the (αhv) 1/n vs. hν graph.[24]

CONCLUSION

Research into CdSe core/shell Nano crystals distributed in PVA reveals an encouraging approach to the development of long-lasting, economical, and energy-efficient optoelectronic devices. Nano crystals with a core-shell structure show improved stability, adjustable emission, and high photoluminescence efficiency by taking use of the quantum confinement effect and surface passivation. Their inherent qualities are preserved when they are incorporated into a transparent and flexible host matrix, such as PVA, while their film-forming capabilities, environmental resistance, and mechanical strength are enhanced. Optical and electrical characteristics of CdSe-PVA Nano composites work together in a way that opens up a world of possibilities. Among them are more sensitive photodetectors, solar cells that absorb more light, and light-emitting diodes that produce more pure colors. In addition, PVA-based composites are compatible and scalable, so they may be mass-produced at cheap cost, meeting the rising need for wearable and flexible electronics. Finally, next-generation optoelectronics may benefit from a flexible platform made possible by integrating CdSe core/shell Nano crystals into PVA, which overcomes the drawbacks of bare Nano crystals. Nano crystals will get from the lab to the real world faster if researchers keep working to improve their design, dispersion methods, and device topologies.

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