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Investigation of CdSe Coatings for Solar Cell Application

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Abstract: Cadmium Selenide (CdSe) quantum dots were synthesized using a solution-based method which was cost effective and environmentally friendly. The synthesised quantum dots were subsequently spin coated on glass substrates with a spin coater at varying coating speeds to form CdSe thin films. The optical characteristics of the thin films, such as absorbance and transmittance, were then studied using a UV-Vis Spectroscopy. Based on the absorbance spectrum and using the Tauc relation, the quantum dots were estimated to be in the size range of 2.9 nm. The transmittance spectrum shows a minimum of 50% transmittance which is in the range required for the CdSe thin films to be utilized as a window photovoltaic system. The results suggest that high transmittance may be achieved using spin coating, which is a low-cost process for producing thin coatings on window panes. Thermal and photostability tests were performed on the CdSe thin films after they were annealed at 150 °C for 4 hours. Another round of optical characterization were done after the stability tests to observe the physical durability of the quantum dots. However, the optical properties such as the transparency and absorption of the CdSe thin films were found to be affected after the realistic test. This might be attributed to the oxidation-induced degradation of the CdSe quantum dots. This can be further improved by further treatment of the coating or by coating the CdSe quantum dots with a shell. The high transparency CdSe coatings obtained can be utilised in solar cell applications.

Keywords: CdSe, Quantum Dots, Spin Coating, Optical Properties, UV-Vis

1. Introduction

Quantum dots (QDs) have been extensively researched for usage in a variety of applications including photovoltaics, biomedical, optics, telecommunications, and many more. It is a currently qgrowing subject, and numerous studies are being conducted to learn more about it in order to improve its use in a variety of different applications. As a result of its outstanding features such as adjustable bandgaps and better optical properties, quantum dots have been regarded as the next generation of semiconducting materials [1,2].

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Based on quantum confiment effect which is present in quantum dots the size of the particle impacts the band gap of the material, The band gap between the highest valance band and the lowest conduction band increases as particle size decreases. As a result, it takes more energy to excite the particle. However, as the particle returns to its resting condition, greater energy is released [3]. Due to the large amount of energy that will be released while returning to the ground state, smaller quantum dots particle size are preferable.

Cadmium Selenide (CdSe) marks out there as a standout material among the recorded semiconductor QDs because it allows for large tuning of its optical band gap to span the entire visible spectrum by varying particle size [4]. The standard bandgap of CdSe is 1.74 eV and normally, variations in the bandgap are generated by the quantum confinement effect in quantum dots. CdSe quantum dots has been studied to be used as a thin film on windows in order to reach acceptable efficiency on window photovoltaic systems at low cost [5]. The method by which energy from the sun falls on the window and is absorbed by the CdSe thin layer deposited on the glass before being directed to solar cells at the window's edges to create electricity. By adjusting the particle size of the quantum dots, we can engineer the energy range of absorption to enhance the solar cells efficiency.

The synthesis of CdSe quantum dots has particularly been difficult due to the usage of trioctylphosphine in the synthesis, which is extremely hazardous if breathed or comes into touch with skin and is toxic to the environment. As a result of prior research, CdSe was successfully produced by the aqueous non-triocytlphosphine approach. This technique of synthesis is environmentally favourable, and CdSe may be manufactured in a simple and safe manner. There are several techniques for producing thin film coatings on glass substrates using synthetic CdSe. Spin coating is one of the quickest, easiest, and most cost-effective methods [6]. The spin coating process is controlled by characteristics such as solvent evaporation rate, velocity of the spinning substrate (spin rate), and coating solution viscosity [7].

The optical property necessary to create a clear solar panel is transmittance. To achieve transparent solar panels, a minimum of 50% transmittance and above is necessary [8]. The Ultraviolet-Visible Spectroscopy is one of the most effective methods for studying the transmittance properties of CdSe thin films. In this work, a non-hazardous CdSe was synthesised and then spin coated on a glass substrate to form a transparent film that has the potential to be utilized in the application of transparent solar panels. Although quantum dots offer outstanding properties such as unique size dependent band gap tunability due to the quantum confinement effect, their physical durability is susceptible to heat and photostability [9]. The relevance of testing the physical endurance of thin films under stress-free and harsh conditions allows us to better understand the stability of quantum dots in that state. Hence, the stability of the quantum dots in terms of physical durability is also equally important as the transmittance and it is also looked upon in this study.

2. Materials and Methods

The CdSe quantum dots were made using an aqueous technique and then spin coated on glass substrates using LAURELL WS-400-6NPPS spin coater. The parameters of the spin coating were varied to investigate the effect of the spinning substrate's velocity on the optical characteristics. UV-Vis spectroscopy (Shimadzu UV-3600 plus) was used to characterise the optical characteristics of the CdSe thin films that were produced. Stability tests were performed to determine the physical durability of the manufactured samples.

2.1 Chemicals and Apparatus

Selenium powder (99.9%), Cadmium Oxide (99.9%), Oleic acid (analytical grade), paraffin liquid (chemical grade), and hexane (analytical grade) were all acquired from Sigma Aldrich, with the exception of hexane, which was purchased from Fisher Scientific. The following equipment was used in this experiment: a 3-neck flask, a magnetic heater/stirrer, droppers, beakers, and a thermometer.

2.2 Sample Preparation and Characterization

Separately, the Se and Cd precursors were prepared, and 2.5 ml of the Cd precursor was injected into the Se precursor. To obtain the lowest quantum dots size range feasible, the CdSe was extracted immediately from the combined solutions. The glass substrates (2.5cm × 2.5cm) were washed with detergent, cleaned with absolute ethanol and acetone, and dried in an oven at 80 °C for 10 minutes. The substrates were then spin coated at 1500 rpm, 2500 rpm, 3500 rpm, 4500 rpm, and 5500 rpm to form CdSe thin films. Field-emission Scanning Electron Microscopy (FESEM) was used to examine the sample's surface morphology while UV-VIS Spectroscopy was used to analyse the spin coated samples to determine how the speed influenced the optical characteristics of the samples. The optical band gap and particle size of the CdSe quantum dots produced was determined using absorbance data from the first round of characterization. Following the initial phase of characterization, the samples were examined for heat and UV radiation stability. There were two sorts of testing performed. The first was a stress-free test, followed by a realistic test. Following each test, characterisation of the samples was performed to examine the changes in optical properties of the samples to see whether they were changed by any of the circumstances. The stress-free test conditions were 100 hours of 25°C heating and UV radiation (365nm). The realistic-test circumstances were a bit harsher, with the samples subjected to 85°C and UV radiation for 200 hours.

2.3 Equations

Using the Tauc relation, the relevant bandgap energy may be calculated from the commencement of absorbance using the UV-Vis spectra, as indicated in Equation 1

$$\alpha h\nu = \mathrm{A}(h\nu - EQDs)\mathrm{n} \qquad \text{Eq 1}$$

Where α is the coefficient of absorption, hv is the photon energy, *A* is a constant and n is (1/2) for allowed direct transitions and (2) for indirect transitions, *Eg* is the optical band gap [9]. The quantum dots size was determined using the effective mass approximation (EMA) model given by Brus based on these bandgap energy values, as stated in Equation 2.

$$E_{\mathrm{QDs}} = E_{\mathrm{bulk}} + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \qquad \text{Eq 2}$$

The CdSe bulk bandgap energy given is 1.74 eV, the value of me ∗ is 0.13 *me*, and the value of mh ∗ is 0.45 me where me is the mass of electron, *Eg* and bulk *Eg* are the energy gap of nanoparticle and bulk respectively, *h* is the Planck constant and *R* is the nanoparticle radius

3. Results and Discussion

Figure 1(b) shows the magnification of 500 × coated glass exhibited pinhole-like structure all over the surface of the substrate when compared to 500 × magnified empty glass in Figure 1 (a). When the surface was magnified further as viewed in Figure 1(c), spherical-shaped dots were seen, and further magnification (10,000 ×) of the dots showed a snowflake-like structure seen in Figure 1 (d). The equally dispersed spherical shaped dots imply that the glass substrates had a uniform and homogenous coating, however the lack of dots on the surface might be due to CdSe dilution in hexane. The dilution was performed to lower the viscosity of the CdSe solution in order to facilitate the spin coating process. A dark region around the snowflake-like structure in Figure 1(d) shows that the CdSe is being capped by oleic acid, inhibiting further agglomeration.

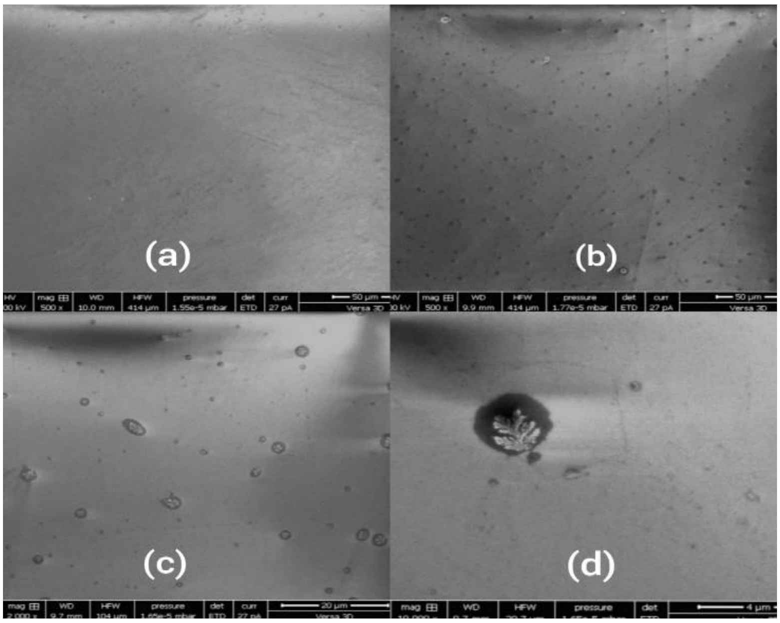

Figure 1 : (a) 500 × magnification of empty glass substrates, (b) 500 × magnification of CdSe coated glass substrates (pin hole-like structure), (c) 2000 × magnification of CdSe coated glass substrate (spherical shaped dots) and (d) 10,000 × magnification of CdSe coated glass subtrates (agglomeration viewed).

The optical transmittance spectra of five samples annealed at 150 °C for 4 hours and measured with a UV-spectrophotometer at wavelengths ranging from 200 nm to 800 nm for varied coating rates are shown in Figure 2. The film's transmission values may be demonstrated to be low at short wavelengths (<380 nm) and high at long wavelengths. This implies that the film functioned as a transparent material at long wavelengths. At a spin speed of 3500 rpm, the average transmittance value is 70%. It is worth noting that high transmittance is one of the most important characteristics of visible window materials. All CdSe films seemed to be quite transparent in the visible region. The thickness of the film decreases as the coating speed of the CdSe thin films increases, improving the transmittance of the CdSe films. As a result, we can see an increase in sample transmittance from 1500 rpm to 3500 rpm, as anticipated. Although higher speeds produce greater transmittance, it was reported that lower speeds provide a thicker and more compact film surface with enhanced crystallinity [10].

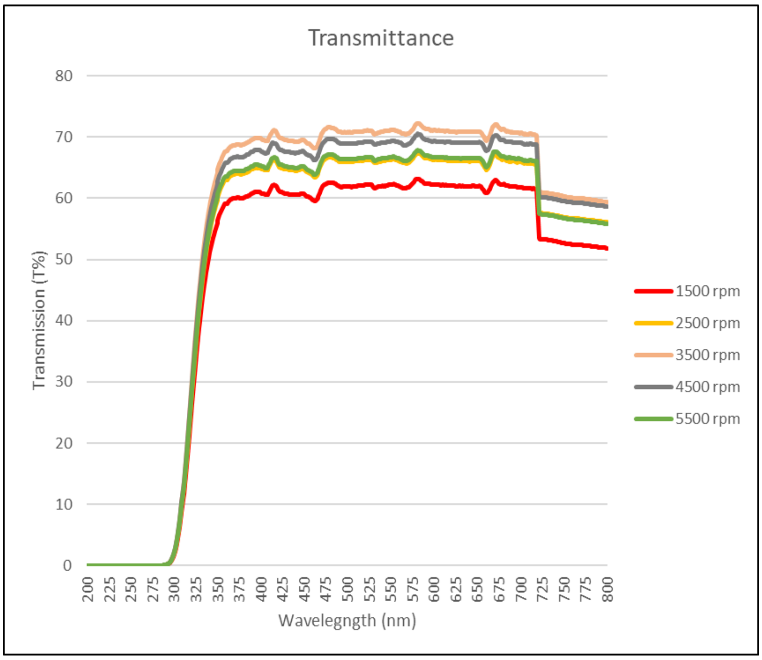

Figure 2 : Transmittance spectra of CdSe thin films at different spin coating speed.

The absorption spectra for the films at varied coating speeds are shown in Figure 2. The absorbance of the films diminishes with increasing wavelength and decreasing photon energy. Each sample has an absorption level that does not differ from the others; their sharp absorption edge is displayed at 300 nm, which is related to the fact that CdSe is a direct band gap semiconductor. These results were comparable and similar to the research work of D.A Ajadi et al [9]. We can observe that after 3500 rpm, the sample's absorption capacity increased at 4500 rpm and 5500 rpm. The absorption peak of the CdSe film was not discernible due to a variety of peaks between the wavelengths 380 nm - 660 nm. This is because the time it took to extract CdSe using a dropper ranged from 5 s to 60 s. This might also imply that the sample has a variety of CdSe particle sizes.

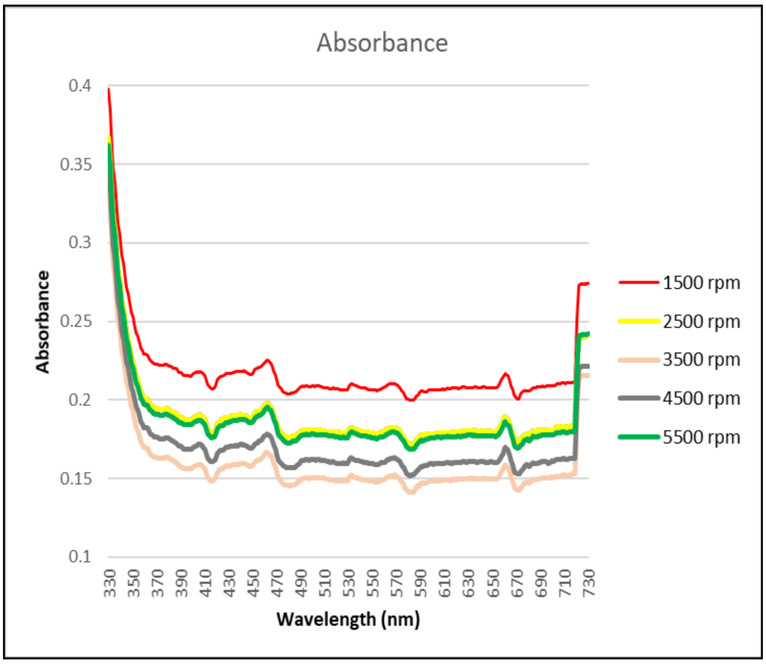

Figure 3 : Absorption spectra of CdSe thin films at different spin coating speed.

Tauc relation based on *Eq 1* was used to calculate the band gap (Eg). The obtained band gap was determined to be 2.81 eV - 2.86 eV as the spin speed increased. The minor divergence in optical bandgap might be attributed to the CdSe thin films' reliance on deposition and processing techniques. There was a drop in band gap for lower speeds, which might be due to an increase in crystallite sizes as spin coating speed is lowered [11].

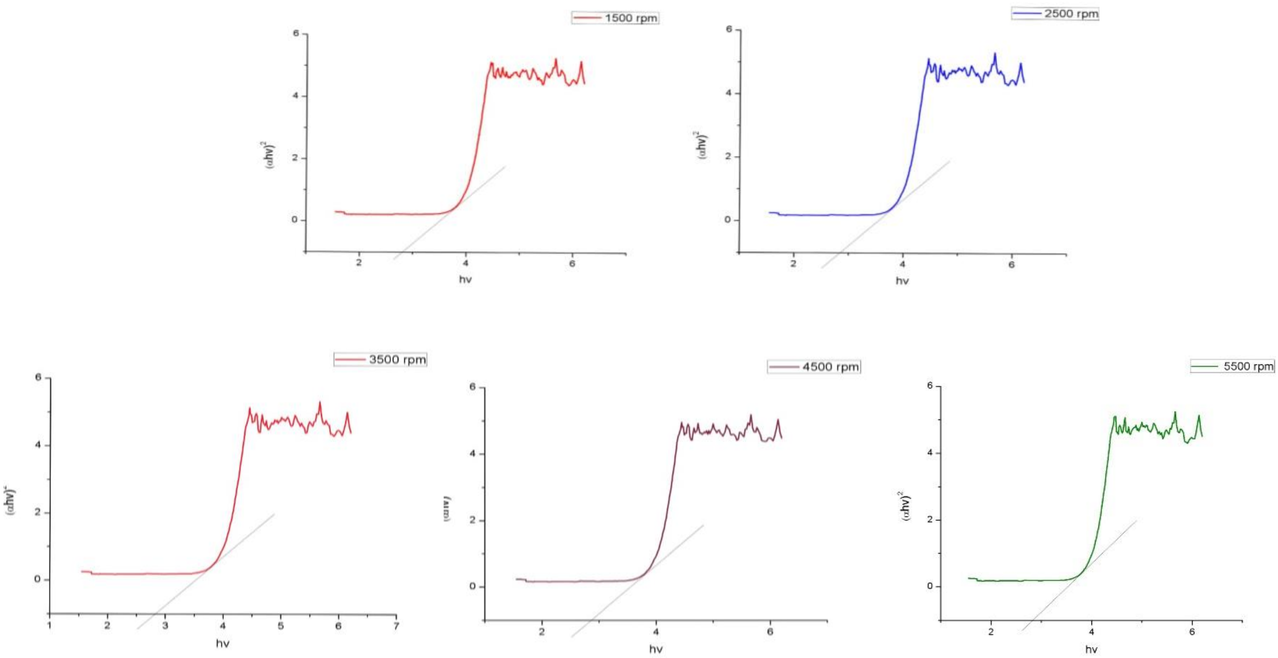

Figure 4 : The graphs represents the relationship between $(\alpha hv)^2$ versus hv (eV)

The quantum dots size was approximated using Brus' effective mass approximation (EMA) model, as indicated in *Eq 2*, based on the bandgap values inferred from the graph. Table 1 shows the particle size distribution of CdSe, which is quite comparable to the findings of (G.R Amiri et al., 2013) [2]. The grain boundary, stress, and interaction potentials between defects and the host materials in the films create the difference in band gap between the thin film and bulk CdSe.

Table 1 : The table demonstrates a trend of particle size reduction as spin speed increases.

Spin Speed (rpm)	Band Gap (eV)	Radius (nm)	Particle Size (nm)
1500	2.81	1.480	2.96
2500	2.83	1.475	2.95
3500	2.83	1.475	2.95
4500	2.84	1.465	2.93
5500	2.86	1.450	2.90

The stress-free stability test was carried out for 100 hours at room temperature and UV irradiation (365 nm). Based on Figures 5 and 6, the optical characteristics of the sample remained constant, implying that the samples did not degrade during the stress free test. There were no influence of temperature or UV radiation on the samples. The stress-free test shows that CdSe thin films are stable and do not degrade in the best-case scenario environment.

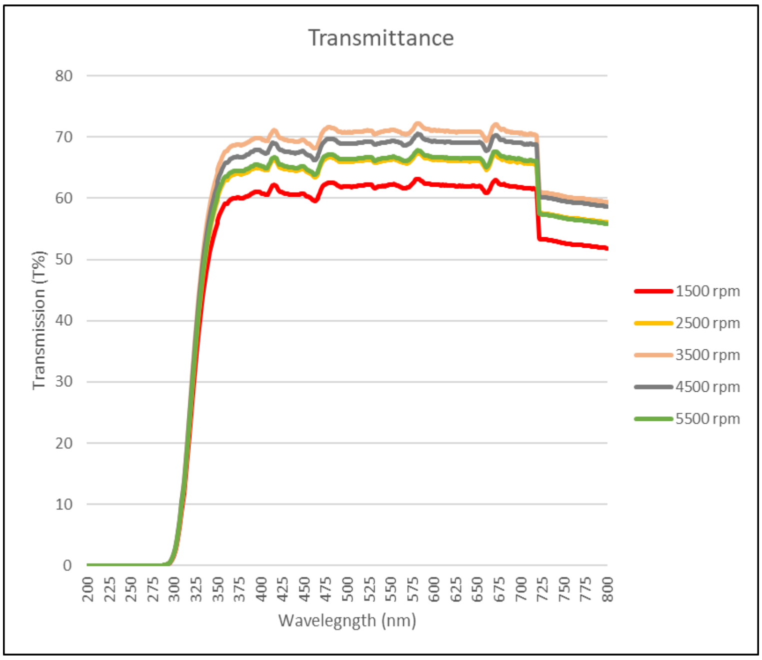

Figure 5 : The graphs show no changes in transmittance when the CdSe thin films were subjected to a stress-free test to determine their physical durability.

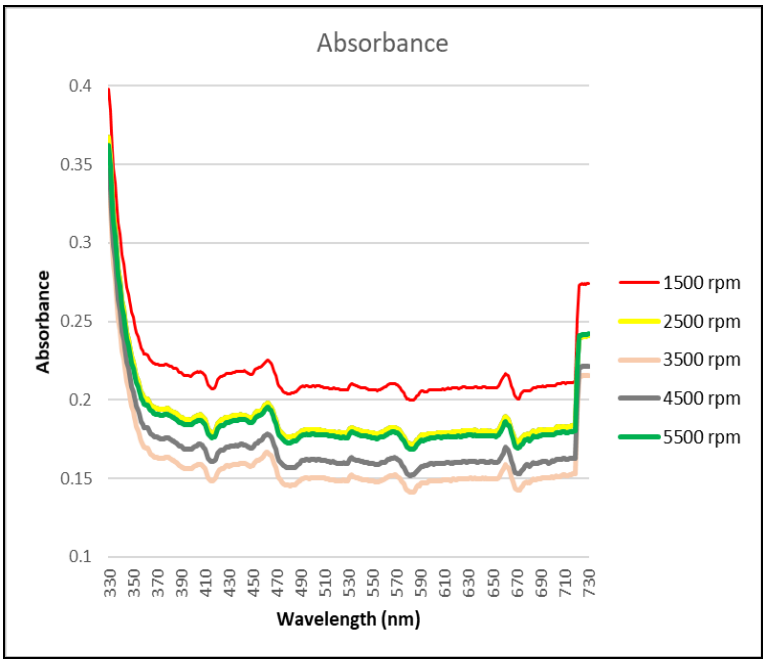

Figure 6 : The graphs show no changes in absorption when the CdSe thin films were subjected to a stress-free test to determine their physical durability.

Based on the figure 7, the optical transmittance of the samples were reduced to 80%. The sample that was spin coated at 3500 rpm showed the highest transmittance and lowest absorption spectrums. While the sample spin coated at 1500 rpm remains the lowest transmittance and highest absorption. The absorption peaks of all the samples, on the other hand, were not distinguishable, as observed in the first two sample characterizations.

The decrease in transmittance might be attributed to oxidation caused by prolonged exposure to high temperatures (85 °C), which increases the rate of oxidation to increase, as well as photooxidation caused by prolonged exposure to UV radiation (365 nm). Continuous exposure to ambient air causes irreversible loss of optical characteristics. Long-term air exposure causes surface trap states, which result in a permanent reduction in sample transmittance [12].

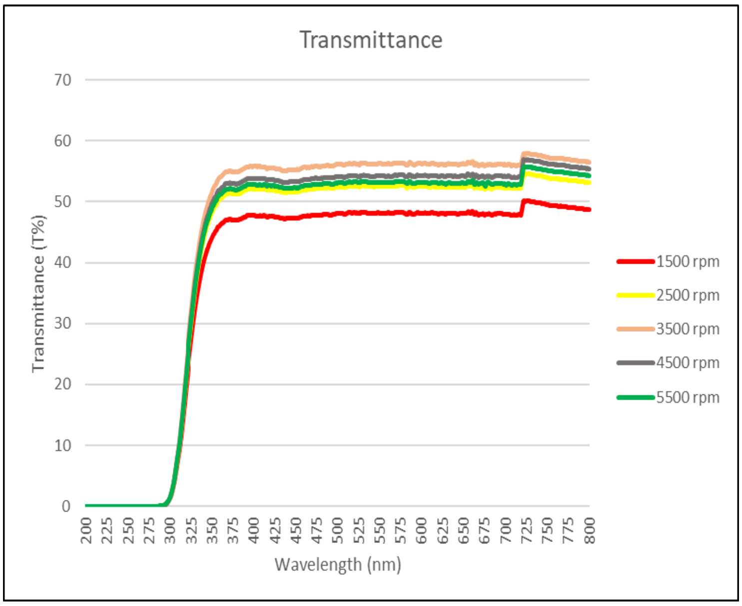

Figure 7 : The graphs shows a decrease in transmittance spectrum when the CdSe thin films were subjected to a realistic test to determine their physical durability.

The absorption spectra of the samples increased overall after 200 hours of exposure to UV light and high temperature. The samples show a decline in absorption properties from 1500 rpm to 3500 rpm, followed by a slight increase at 4500 rpm and 5500 rpm. This may be due to the fact that the size of the crystallites increases with film thickness, and bigger crystallite sizes give more empty inter-granular space, resulting in a higher absorption coefficient [13]. Although it has been widely stated that quantum dots are stable in harsh conditions. When they are not encapsulated, they are quickly oxidised. Hence, these outcomes are expected and can be enhanced with further measures.

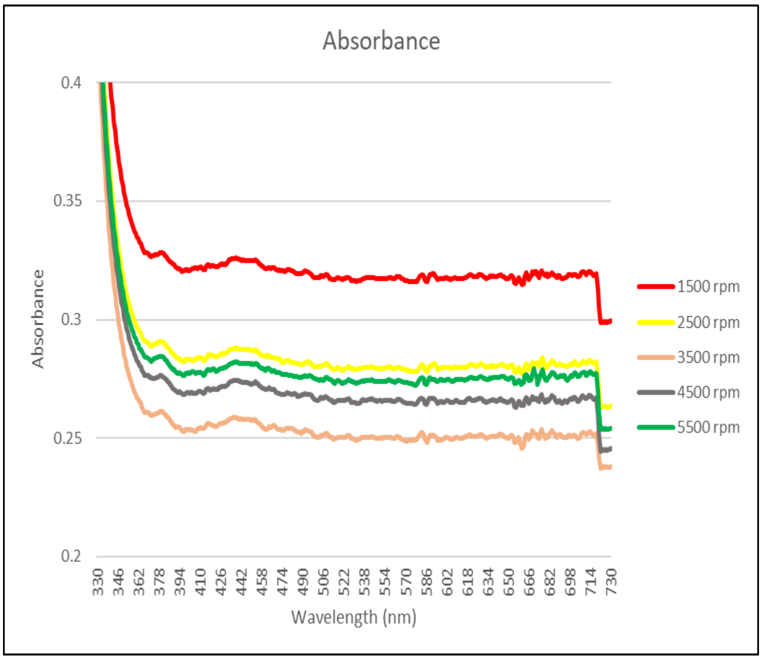

Figure 8 : The graphs shows an increase in the absorption spectrum when the CdSe thin films were subjected to a realistic test to determine their physical durability.

4. Conclusion

The solution-based technique, which is less hazardous and safer for the environment, can be used to synthesise small particle sizes of CdSe quantum dots. The bandgap of the CdSe quantum dots were estimated using Tauc's Relation and the obtained value was 2.81 eV-2.86 eV. There was a blue shift observed when compared with the bulk CdSe bandgap 1.74 eV(720 nm) due to the quantum confinement effect present in CdSe quantum dots.

A rather uniform CdSe thin films on glass substrates was achieved using a simple and low-cost spin coating method. The structural features of the thin film using spin coating method demonstrate a uniform and homogeneous coating. However, embedding quantum dots in polymer matrices can improve their stability and prevent agglomeration, allowing the dots to stay the same size and generate the same attributes without losing any. The optical properties are dependent on the spin coating speed; increasing the coating speed enhances the transmittance property. In this investigation, the best optical property obtained was a spin speed of 3500 rpm for 60 seconds. Where the transmittance is at least 70%, this is ideal for the usage of window solar panels.

CdSe thin films are stable under typical circumstances and can be utilized without degradation. Nevertheless, when exposed to high temperatures and UV light over an extended period of time, the quantum dots degrade. The stability of QD films can be improved by modifying the ligands and encapsulating the QDs in polymer matrix. Strong covalent bonds between the polymer matrix and the

QDs are the best way to improve their oxygen and moisture stability, photostability, and thermal stability.

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