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Radioluminescence and optic characterization of CdSe quantum dot added polymer nanocomposites

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Abstract

In this study, CdSe quantum dots which is highly luminescent were synthesized by two phase method using oleic acid (OA) as a surfactant. New nanocomposites have been obtained by mixing CdSe quantum dots with low-density polyethylene (LDPE) in different ratios. The structural (FT-IR), morphological (TEM, SEM), thermal (TG-DTA) and absorption (UV-VIS) properties of these nanocomposites were investigated as well as their radioluminescence (RL) properties. Radioluminescence peaks at 335 nm, 510 nm and 655 nm for the oleic acid-capped CdSe nanocrystal were observed. As a consequence of the nanocomposites being doped with powder CdSe quantum dot, a significant blue shift was observed in the absorption bands. The optical band gap for CdSe was calculated as 1.82 eV. The nanocomposites blended with CdSe QD, this value increased to 3.23 eV.

Keywords: *Quantum dots, Radioluminescence (RL), Low Density Polyethylene (LDPE), optical absorption, structural characterization, thermal analysis.*

CdSe kuantum nokta katkılı polimer nanokompozitlerin radyolüminesans ve optik karakterizasyonu

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Özet

Bu çalışmada, yüksek parıldar madde olan CdSe kuantum noktalar, yüzey aktif madde olarak oleik asit (OA) kullanılarak çift fazlı yöntemle sentezlenmiştir., CdSe kuantum noktalarının alçak yoğunluklu polietilen (AYPE) ile farklı oranlarda karıştırılmasıyla yeni nanokompozititler elde edildi. Bu nanokompozitlerin yapısal (FT-IR), morfolojik (TEM, SEM), termal (TG-DTA) ve soğurma (UV-VIS) özelliklerinin yanı sıra radyolüminesans (RL) özellikleri araştırıldı. Oleik asit kaplı CdSe nanokristali için 335 nm, 510 nm ve 655 nm'de radyolüminesans pikleri gözlendi. Nanokompozitlerin toz haldeki CdSe kuantum nokta ile katkılandırılması sonucu, soğurma bantlarında önemli derecede mavi bölgeye kayma gözlemlendi. CdSe için optik bant aralığı 1.82 eV olarak hesaplandı. CdSe QD ile katkılandırılmış nanokompozitler için bu değer 3,23 eV'ye yükselmiştir.

Anahtar kelimeler: *Kuantum nokta, Radyolüminesans (RL), Alçak Yoğunluklu Polietilen (AYPE), optik soğurma, yapısal karakterizasyon, termal analiz.*

1. Introduction

Quantum dots have become an important focal point of science thanks to their electronic and optical properties, which have been used in many different applications today. These are often preferred in semiconductor technology due to their controllable nano size, strong emission characteristics and high absorption values [1–3]. Especially due to its controllable dimensions, from medicine and biotechnological applications according to their emission behavior, to imaging and hybrid solar batteries, has become widely used in many fields [4]. Another interesting material that has recently been widely used is nanocomposites. The small volume of nano-sized additive materials means that they have a very large surface area. Thus, the superficial properties of the nanocomposite material directly influence the physical and chemical properties of the matrix [5]. Therefore, nanocomposites have attracted considerable interest in the industrial and technological field owing to their remarkable morphological, mechanical, thermal, optical and other remarkable changes [6].

The nanocomposites prepared by incorporating the quantum dots into low-density polyethylene at a very low rate have been found to have the same luminescence characteristics as the powder quantum dot. It has been observed that these nanocomposites with quantum dot additive have significant advantages in experimental studies in terms of being easy to shape, being flexible, being able to prepare in desired quantity and size and having more suitable storage conditions. [7].

The CdSe quantum dot prepared by the synthesis method in the two-phase method was doped into low density polyethylene (LDPE) and polymer nanocomposites were prepared by solution blending method.

In this study, the optical absorption spectra of composites which are consisted of three polymer nanocomposites prepared with CdSe adding and a pure LDPE composite were obtained, and the band gap energy values of samples were calculated from these spectra. Unlike other quantum dot studies, the RL system was used in obtaining emission spectra. It is possible that these RL spectra can be obtained for solid, colloidal or powder samples. This is a significant advantage in terms of ease of analysis. However,

in the fluorescence system, which is frequently used in the quantitative analysis of quantum dots, the material can only be examined in the colloid structure. If the sample is solid, it should be dissolved in certain molarities with solvent. The photoluminescence and fluorescence spectroscopy, which are used to determine the emission characteristics of quantum dots, are usually induced by low energy sources. The RL system, in which high-energy X-rays is used as excitation source enables the detection of sputtered electrons by inducing electrons in deep traps in semiconductor nanocrystals. This is a significant advantage of the RL system [8, 9].

2. Materials and method

2.1 Synthesis of CdSe nanocrystal

CdSe nanocrystals were synthesized by the two phase method [10, 11]. 0.4 g of cadmium myristate as a cadmium source, 2 g of oleic acid as a surfactant is dissolved in 80 ml of toluene at a temperature of 80°C and kept for later use in the process. In a further step, 80 ml of distilled water is heated to 100 °C under nitrogen and 1 ml of NaHSe is injected into the reaction flask. The temperature was kept constant at 100 °C. Nitrogen saturation was provided, and the toluene phase solution was added to the water phase with the aid of a stirrer. CdSe quantum nanocrystals begin to form at the interface in about 30 minutes. During the process, growth and optical properties of nanocrystal were controlled by UV-Vis, taking samples at different intervals. The reaction is stopped when the desired size is obtained according to the absorption spectra. The biphasic mixture in the reaction flask is separated using a separatory funnel.

2.2 Preparation of QD added polymer nanocomposites

In the heater with the temperature stabilized at 130 °C, the weighed low-density polyethylene granules were heated to the required softness in the borosilicate glass beaker. The weighed powder quantum dots were completely dissolved by stirring in 20 ml of toluene. This solution is incorporated into the molten polyethylene. Toluene is a good solvent in polyethylene material too. 20 ml of toluene in the solution provides even better dissolution of the polyethylene [12]. The mixture was stirred at 130 °C. for 10 minutes to remove toluene from it. Then, the mixture was to cool down to room temperature and allowed to stand for at least 48 hours. The toluene residues that may be present at this point have been removed from the acceptable level. 0.30 g of the dried mixture was weighed and again softened by heating at 110 °C for 15 minutes at the melting point of polyethylene. Thus, more homogeneous and smoother composites are obtained by pressing. The sample is cooled to room temperature under a pressure of 10 MPa. The nanocomposites with a smooth surface of 1.5 mm thickness and 16 mm diameter were obtained.

For the radioluminescence (RL) measurements of the CdSe QD and nanocomposites, excitation was made with a Machlett OEG-50A X-ray tube operated at a maximum experimental level of 30 kV and 15 mA. Luminescence detection system is conducted with a Yobin Yvon spectrometer, coupled to a liquid nitrogen cooled CCD detector. The fluorescence spectra of CdSe QD were recorded by Agilent Technologies Cary Eclipse Spectrophotometer at 290 nm excitation wavelength. Optical absorption spectra of QD and nanocomposites were recorded at room temperature in the wavelength region of 200–2000 nm using Perkin-Elmer Lambda 950 spectrophotometer. TEM images were obtained using a FEI Tecnai G2 -Biotw Spirit High Contrast Transmission

Electron Microscopy and operated with Lanthanum hexaboride (LaB_6) electron gun, under accelerating voltage in the range of 20-120 kV. The FTIR spectra were recorded in the region 4000–650cm^{-1} using an Agilent Technologies Cary 660 Spectrometer with room temperature. The thermal analysis (TG-DTA) of samples was performed Hitachi SII Exstar 7300 thermal analyzer. The thermal behavior of nanocomposites was studied in the temperature range of 25–575 ^{o}C at a heating rate of 10$^{o}min^{-1}$in air atmosphere. Scanning electron microscopy (SEM) was used to examine the morphology of nanocomposites by using a Philips XL-30S FEG e SEM.

3. Results and discussion

3.1 Optical properties

The radioluminescence measurements of CdSe quantum dot and the prepared nanocomposites were taken with the RL system created by Jobin Yvon monochromator integrated X-ray unit. Figure 1 shows that the powder CdSe and RL spectra of quantum dot added polymer nanocomposites.

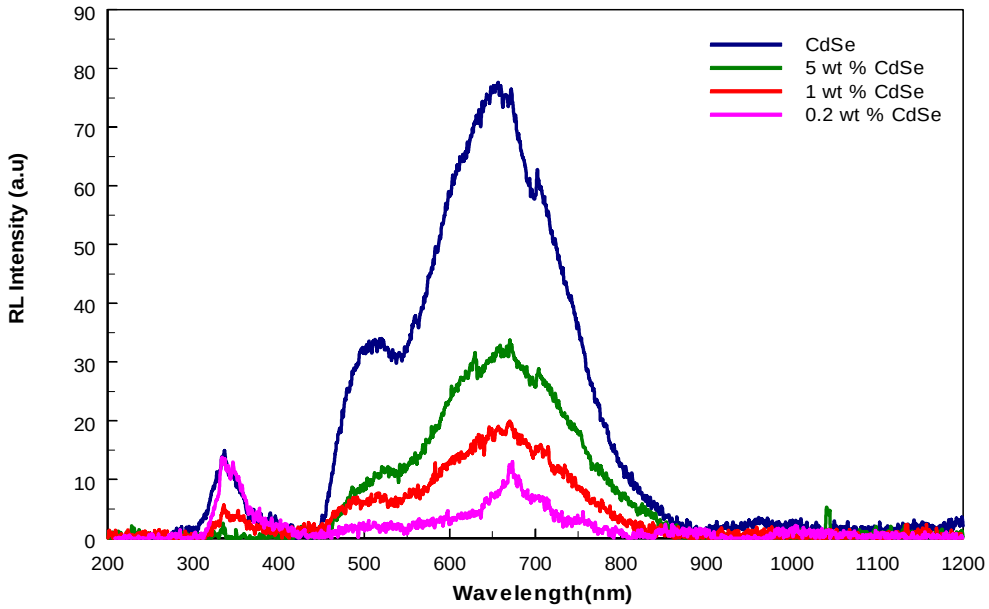

Figure 1. RL spectra of nanocomposites in different ratios (0.2, 1, 5wt%.CdSe) and CdSe QD.

The main radioluminescence peak of CdSe QD is located at 655 nm and there are weak peaks at 335 nm and 510 nm. The peaks at RL spectrum could originate from VSe (Se vacancy), VCd (Cd gap), Se (Se cracks), Cd (Cd cracks). The surfactant (OA), synthesis time and concentration rate are important effect on shifting the peaks red or blue region in RL spectrum.

The decrease in RL intensity upon addition of CdSe QD could be attributed to the charge transfer from polymer to the nanocrystals. This charge transfer results from the formation of separated electron–hole pair that recombines non-radiatively which leads to quenching of emission intensity of nanocomposites. The nanocomposites showed same glow curves with the quantum dot, and the LDPE appears to reduce the RL intensity of the quantum dot.

In figure 2, the low intensity of the emission peak of CdSe, which has a broad fluorescence spectrum, is thought to be caused by surface defects that may occur during the synthesis process. CdSe, which emits around 610 nm (as can be seen in Figure 3 from UV-light images of nanocomposites), has a yellow-orange color in the electromagnetic spectrum.

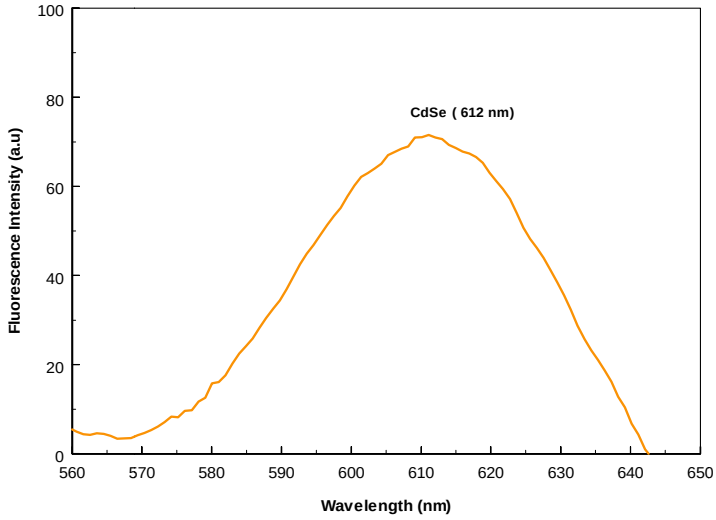

Figure 2. The fluorescence spectrum of OA capped CdSe QD.

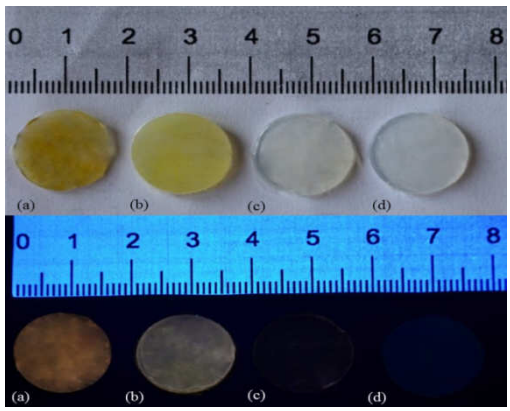

Figure 3. The images of the nanocomposites under UV lamp (λ_{ex}= 365 nm) (a) 5 wt% , (b) 1 wt%, and (c) 0.2 wt% CdSe, and (d) pure LDPE respectively.

In Figure 3, the yellow-orange color, which is apparent in the 5% QD added sample (a), is diminished on the 1% sample (b). At 0.2% QD added sample, it became uncertain that it could only be seen at the edges.

From the figure 4, the optical band gap for CdSe was calculated as 1.82 eV [13]. The absorption spectrum of LDPE showed a significant shift to the red region with the CdSe quantum dot contribution. By increasing the contribution rate, it is seen that forbidden energy band values can be reduced from 3.71 eV to 2.50 eV (Table 1).

As can be seen in Figure 4 when the QD nanoparticles added in LDPE matrix, the absorption band of nanocomposites broadened towards the large wavelengths. The intensity of main absorption bands of the QD added samples increased remarkably. Presumably, this is caused by the radiation-induced rise of quantum dots concentration in polyethylene.

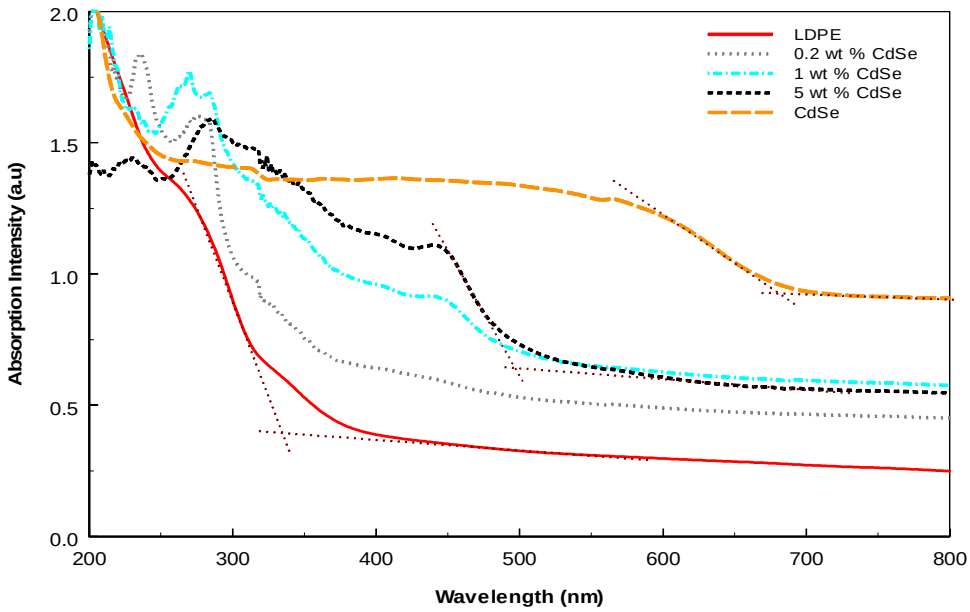

Figure 4. The optical spectra of OA capped CdSe QD and CdSe QD added polymer nanocomposites.

The optical band gap values obtained by using the Eg = hc/λonset equation, where λ is the onset wavelength which can be determined by intersection of two tangents on the absorption edges. Also, λonset represents the electronic transition start wavelength [14].

Table 1. The calculated optical band gap (E_g) and onset wavelength values of CdSe QD, LDPE and, CdSe added nanocomposites.

	LDPE	**0.2 wt %**	**1 wt %**	**5 wt %**	**CdSe QD**
Wavelength (nm)	334	384	492	496	681
Band Gap (eV)	3.71	3.23	2.52	2.50	1.82

3.2 Size determination of CdSe QD

The TEM image and the histogram of the particle size distribution of the OA capped CdSe QD is shown in Fig 5 and Fig 6. The distribution of particle size for CdSe QDs are nearly monodispersed and spherical in shape.

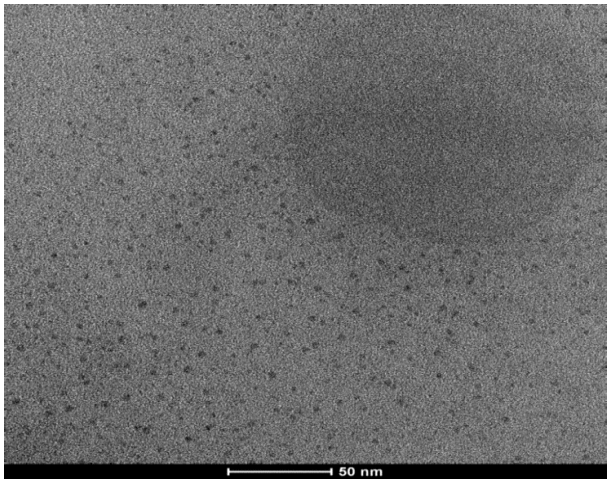

Figure 5. The TEM image of OA capped CdSe QD.

The TEM image of CdSe QD revealed a distinct spherical shape pattern of the particle distribution and also showed that the particles were highly monodispersed and homogenous. The average size distribution of the CdSe QD measured was 2.8 nm.

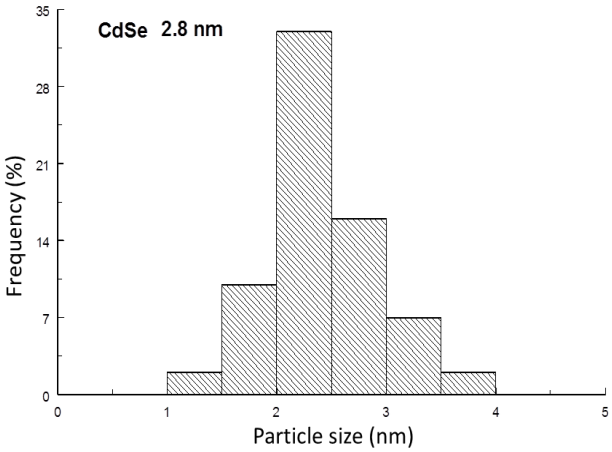

Figure 6. The particle size histogram of CdSe QD.

3.3 FT-IR spectra of QD and nanocomposites

Figure 7 shows the FTIR spectra of CdSe quantum dots and doped nanocomposites. In the spectrum of nanocomposites, it was determined that the absorbance intensity of pure polyethylene showed a decrease with the contribution in the inset spectra at 2800-3000 cm^{-1}. However, it is observed that especially the 0.2% added sample gives a characteristic spectrum by increasing the intensity at values between 700 cm^{-1} and 1300 cm^{-1}. In Fig. 7, the FTIR spectrum of OA capped CdSe QD, there are main peaks at 2850 cm^{-1} and 2920 cm^{-1} which are due to the $–CH_2$ symmetric and asymmetric stretching. The peak at 1420 cm^{-1} is attributed to the OH bending from OA.

In spectra of nanocomposites, apart from the main peaks, there are medium strong peaks refer to the $–CH_2/–CH_3$ bending vibrations at 1460 cm^{-1} and rocking at 720 cm^{-1}. The absorbance intensity decrease shows that CdSe QD which have inorganic structure have been successfully doped inside LDPE which has an organic structure [15, 16].

3.4 Thermal analysis of nanocomposites

The nanocomposites and LDPE show almost the same TG characteristics. [17]. In the TG analysis, the effect of the nanocrystals added in LDPE on the melting rate of nanocomposites was observed.

As can be seen in Table 2, at low addition ratios (0.2% and 1%), nanocomposites show close thermal stability to LDPE. However, the sample with 5% CdSe addition showed faster degradation than the others[18, 19].

Table 2. Thermal degradation values of nanocomposites.

	Degradation Step (^oC)			Residue Weight Percentage		
Sample	T_{start}	T_{max}	T_{end}	**430^oC**	**460 ^oC**	**490 ^oC**
LDPE	184	475	496	16.7	24.41	89.39
0.2 wt %	172	475	499	6.71	23.44	87.19
1 wt %	108	474	494	5.84	23.67	91.85
5 wt %	106	473	496	10.37	26.92	90.84

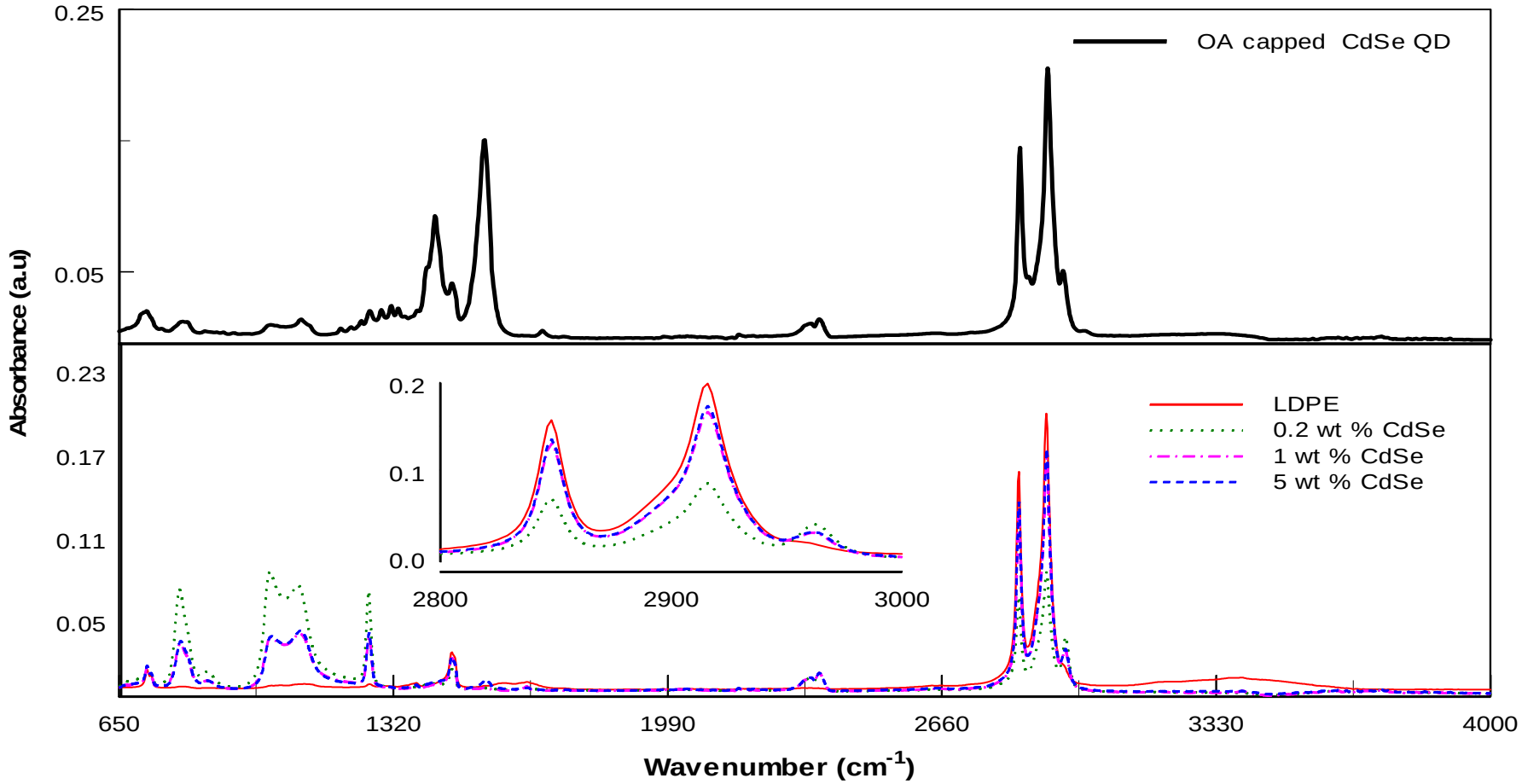

Figure 7. FTIR spectrum of OA capped CdSe quantum dot and FTIR spectra of CdSe doped polymer nanocomposites

The thermal stability of LDPE and CdSe QD added nanocomposites have been investigated. Thermogravimetric curves are given in Fig 8.

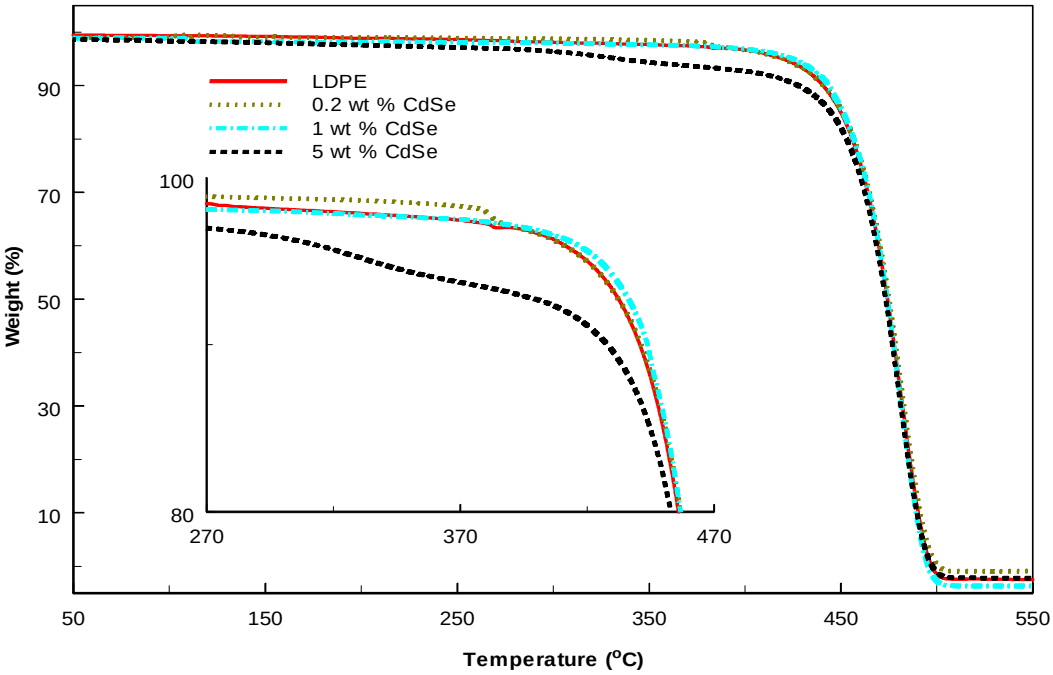

Figure 8. TG curves of CdSe doped polymer nanocomposites.

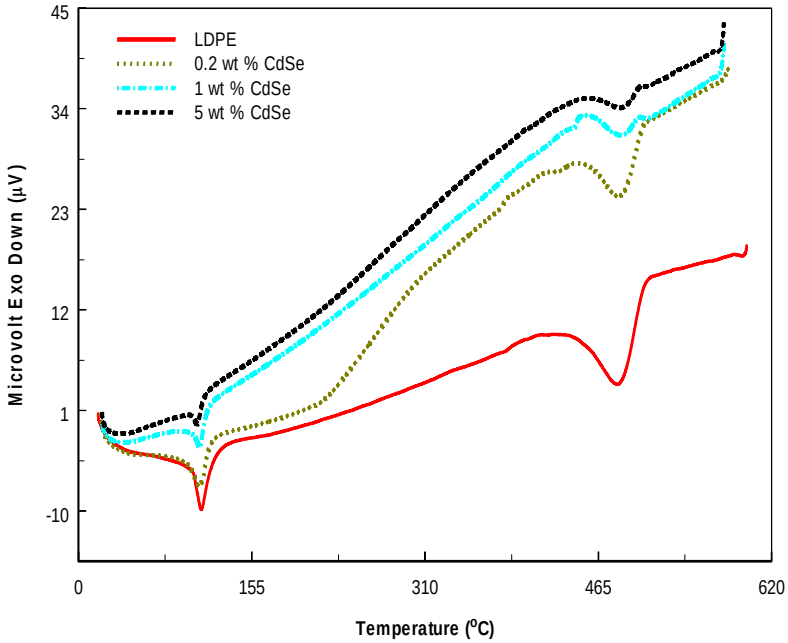

Figure 9. DTA curves of the nanocomposites.

Figure 9, CdSe QD also contributed to the thermal conductivity of the polymer matrix, with the most active being dominant in the 5% CdSe doped sample. the melting point of LDPE was 110 ^{o}C [20, 21], the melting point of the pure polyethylene decreased to 106 ^{o}C due to the quantum dot additive (Figure 10).

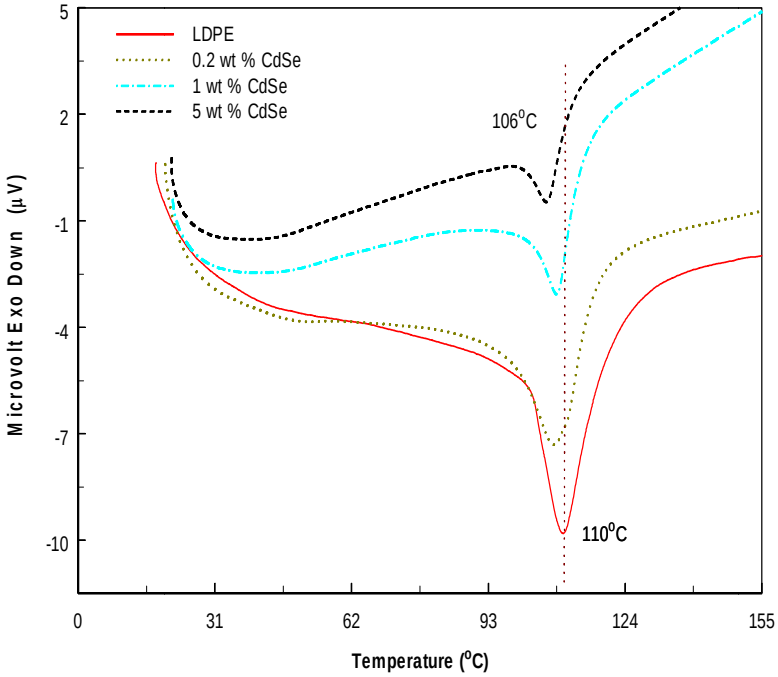

Figure 10. The changing in the melting point of LDPE with quantum dot additive.

3.5 SEM images

Figure 11 also shows irregularly pieced structure in the SEM image. During preparation of the nanocomposites, the powder sample is redissolved in toluene to provide a homogeneous state for QD solution as additive material. Thus, said pieced structure is not a problem in terms of QD homogeneity.

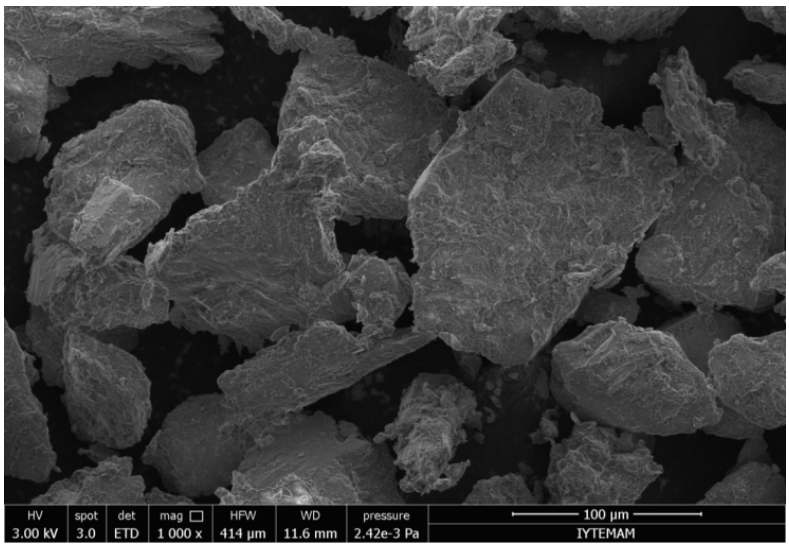

Figure 11. The SEM image taken for oleic acid capped CdSe QD powder.

As shown in Fig. 12, the 100 µm image of 5% QD-doped sample does not have enough zoom to detect quantum dot structures. However, it appears that the surface of the nanocomposite is very smooth. The presence of quantum dots is more pronounced in 5 µm and 10 µm images. The QDs are concentrated in bright circular structures on the surface of the LDPE matrix nanocomposite.

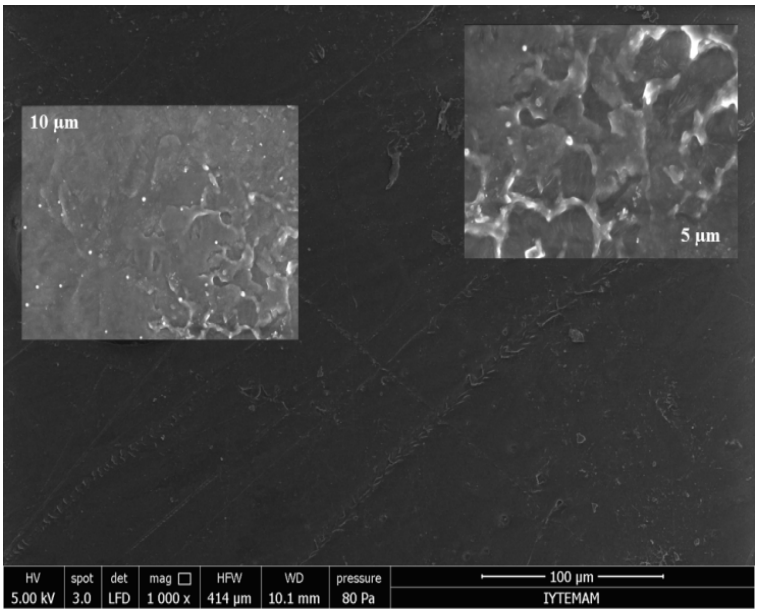

Figure 12. The SEM images of 5 wt% CdSe nanocomposite.

4. Conclusions

The polymer nanocomposites have been prepared with CdSe quantum dots by considering that quantum dots may be an ideal nanocomposite additive due to their high quantum yield and the fact that forbidden energy band spacing and dimensions can be controlled. The optical, structural and thermal properties of LDPE matrix nanocomposites doped with quantum dots at different ratios have been investigated.

It is aimed to determine the advantages of these materials and investigate their suitability for new application areas.

The CdSe QD show a broad fluorescence emission band located at 610 nm under UV excitation (λ=290 nm). RL spectra show that the emission of quantum dots in the polymer matrix have the same wavelength as the powder states. The band gap of OA capped CdSe QD is determined to be 1.82 eV. It was observed that the bandgap of CdSe added nanocomposites increase with the adding ratio of the LDPE. The radioluminescence properties were investigated. In the RL spectrum, three different peaks were obtained at 335 nm, 510 nm and, 655 nm. Also, OA as a surfactant is a significant factor for emission and RL intensity. For the nanocomposites in different ratios (0.2, 1, 5 wt%.CdSe), the decrease in RL intensity upon addition of CdSe nanocrystals could be referred to the charge transfer from polymer to the nanocrystals.

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