J Nanostruct 11(1): 153-164, Winter 2021

RESEARCH PAPER

Synthesis of CdSe and CdTe Quantum Dots: Their Effects on the Znq_2 Luminescence Complex for Organic Light Emitting Diodes

Mohamad Reza Jafari [1,2,*], *Zeynab Sadat Alirahmi* [2], *Davood Ghanbari* [3]

[1] *Department of Physics, Faculty of Physics and Chemistry, Alzahra University, Tehran 1993891167, Iran*

[2] *Department of Physics, Faculty of Science, Arak University, Arak 38156-88349, Iran*

[3] *Department of Science, Arak University of Technology, Arak, Iran*

ARTICLE INFO

Article History:
Received 11 September 2020
Accepted 17 December 2020
Published 01 January 2021

Keywords:
Organic Light Emitting Diode
Synthesis of Quantum Dots
Znq_2 Complex

ABSTRACT

CdSe and CdTe quantum dots were synthesized by a simple hydrothermal method using ammonia and hydrazine in a short time period of 5 hours. In another phase, Znq_2 complex nanostructures were prepared using a green environmentally friendly method, in which saffron extract was used as surfactant. The purity of the nanoparticles was investigated by X-ray diffraction and their dimensions and morphology were studied by scanning electron microscopy. In the next step, CdSe and Znq_2 complexes were synthesized and their synergistic effects on each other was investigated. The photoluminescence results show the luminescence of all three nanostructures in the visible light range, and it was concluded that upon compositing these nanostructures, their luminescence properties remained intact. Their optical and structural properties were investigated using X-ray diffraction (XRD) analysis, infrared spectroscopy (FT-IR), ultraviolet and visible light (UV-Visible) spectroscopy, photoluminescence spectroscopy (PL) and electron imaging (SEM).

How to cite this article
Jafari M.R., Alirahmi Z.S., Ghanbari D. Synthesis of CdSe and CdTe Quantum Dots: Their Effects on the Znq_2 Luminescence Complex for Organic Light Emitting Diodes. J Nanostruct, 2021; 11(1): 153-164. DOI: 10.22052/JNS.2021.01.017

INTRODUCTION

Quantum dots or nanocrystals fall into the semiconductor category of materials. Semiconductors are the basis of new electronics industries and have various applications in apparatus such as optical diodes, display screens, solar cells, and personal computers as well as optical devices in general. The importance of semiconductors is that the electrical conductivity of these materials can be changed by external stimuli such as electric field or light radiation, in order to change them from nonconductors into conductors, so that they can act as a key. This property made semiconductors one of the most important components of a variety of electrical circuits and optical devices.

* *Corresponding Author Email: mo.jafari@alzahra.ac.ir*

Quantum dots, because of their small size, are a unique category of semiconductors. Their diameters ranging from 1 to 10 nanometers, is equivalent to place 10 to 50 atoms next to each other [1, 2]. In these small dimensions, materials behave differently, and this different behavior gives unprecedented capabilities to quantum dots in order to be used in scientific and technical applications.

The quantum dot is an area of a semiconductor crystal that contains electrons, holes, or both in three dimensions. All three dimensions of the material are on a nanometer scale and the main feature of these dots is light emission. The dimensions are so small that the properties of material cannot be justified by the laws of classical

physics anymore. It is only quantum physics that can justify the behavior of material in these dimensions [3, 4].

The nanostructures are composed of 200 to 10000 atoms and their size is equal to a large protein. The structure of quantum dots is typically core-shell. The core, usually made of elements of groups III-V or II-VI of the periodic table, is covered by a shell made of semiconductor compounds. The shell and core are both semiconductors. Semiconductors are materials whose electrical conductivity is in between electrical conductivity of conductors and non-conductors [5, 6].

The efficiency of quantum dots is due to their adjustable wavelength in such a way that they can radiate the most light [7]. The magnitude of this wavelength is strongly influenced by the substance and the size of quantum dots. New methods in nanotechnology have given manufacturers great ability to precisely control the wavelength [8-12].

Upon the development of new materials and methods, the concerns about environmental pollution caused by nanoparticles produced by chemical methods as well as the production of hazardous side products have increased. So, that is important to use green chemistry based methods which are environmentally friendly, clean and non-toxic.In the past, dwarfs, single cells and diatoms were used for green synthesis, but they are less commonly used today because of their high cost of preparation and maintenance. The use of green plants for bio-production of nanoparticles is an exciting and largely unknown possibility. Currently, nanoparticle production using the principles of green chemistry has gained prominence in research. One study in this field is done on the production of nanoparticles using natural materials. Green synthesis methods and the use of natural materials that are beneficial to health and the preservation of the environment, in addition to minimizing the use of chemicals, are also economically cost-effective. Green synthesis methods are also simple and generally single-phase methods, which is a great advantage for doing research and saving time [13-21].

We also attempted in this study, to take a step further in this area of science. Due to the importance of environmental preservation and green chemistry, the required Znq_2 was green synthesized. After preparing the desired quantum dots, their effect on green synthesized Znq_2 is to be investigated.

MATERIALS AND METHODS

Materials

Zinc nitrate 4 hydrate, Quinoline (C9H6NO), saffron extract, tellurium chloride, cadmium nitrate, hydrazine, ammonia, deionized water, laboratory containers such as beaker, balloon, pH meter, magnetic stirrer and mixer, oven, centrifuge, autoclave and nitrogen gas source

Green synthesis of Znq_2

An extract is a substance obtained from a material, plant or fruit applying distillation, squeezing or boiling, or by the aid of a solvent such as water or alcohol. In general, extraction is carried out in two ways of using heat and without using heat. If the material inside the plant is heat sensitive, it is better to use the second method in which we don't use heat. Extraction using heat is the faster and cheaper method, in which we use an apparatus called Soxhlet. Soxhlet apparatus is constructed in different sizes to extract different amounts of plants. The apparatus consists of four parts: heat source, balloon, the device and refrigerant. We can extract from a couple of grams to several kilograms of plant powder at the laboratory level by using this apparatus. To do this, mix the dried and milled plant in a suitable beaker with the desired solvent and place it in the Soxhlet chamber when it comes to a paste. Then we put the balloon in the electric heater and fix it with a clamp.

After adding the solvent from the top of the Soxhlet, place it on the refrigerant, open the water pipe, then turn on the electric stove and adjust the heat so that the solvent inside the balloon boils evenly. Extraction may take from 5 to 50 hours depending on the plant type, solvent type and the amount of plant. After the extraction is completed, we will flow the liquid extract inside the balloon through the funnel and filter paper and then use it in accordance with the instructions [11].

In this synthesis the ratio of zinc and Quinoline is 1:2. To do this, we dissolve $ZnNo_3$ in a vessel containing 100 ml of water and separately dissolve quinoline in a vessel containing 100 ml of water, and place them on a magnetic stirrer for 1 hour to be dissolved well. Then mix both solutions in one container and add 0.5 ml of saffron extract and place container on a magnetic stirrer for 1 hour to achieve a uniform, green-yellow solution. Then we transfer the solution to the autoclave and place it in the oven at 150 °C for 15 hours. After 15 hours,

we switched off the apparatus and after cooling the autoclave, the solution was transferred to another container to be centrifuged and precipitate. Then we rinsed precipitate with deionized water and placed it at 70 °C for one day to be dried.

CdSe quantum dot synthesis

We need a source of selenium to do this, so we use selenium chloride ($Secl_4$) in here. The sources of cadmium are also cadmium nitrate (Cd $(No_3)_2$), ammonia (NH_3H_2o), hydrazine, deionized water Required equipment: Laboratory containers including beaker, balloons, etc., litmus paper, magnetic stirrer, oven, centrifuge and autoclave, nitrogen gas source First, we dissolve cadmium nitrate and ammonia in 100 ml of water and place it on magnetic stirrer for 1 hour to obtain a clear solution. Then we dissolve selenium chloride and hydrazine in 100 ml of water and place it on magnetic stirrer for 1 hour to obtain a clear solution. After one hour, we mixed both solutions into a three-spout balloon, and while one of the spouts was closed, nitrogen gas added the solution from the other two spouts. We transfer the solution into the autoclave after 4 hours. Then we placed the autoclave into an oven at 180 °C for 5 hours. After 5 hours, the apparatus was switched off and the autoclave was removed and the solution was transferred to another container after being cooled, then it subjected to centrifuge to remove the precipitate and was washed several times with deionized water. Finally, the precipitate was placed at 50 °C for 1 day to be dried. Then the synthesized quantum dots were ready to be analyzed and identified.

Synthesis of CdSe complex using Znq_2

In order to synthesize the cdSe and Znq_2 complexes we need both materials that we synthesized in the previous step. Now we use them to synthesize the desired complex. To do this, we dissolve 1 ml of cdSe in 100 ml of water and 0.1 g of Znq_2 in 100 ml of water. After 1 hour, we mix the two solutions, then place them on a magnetic stirrer for 1 hour to obtain a uniform solution. After these steps, we transfer the prepared solution into an autoclave and place it in the oven at 150 °C for 24 hours to prepare the desired complex. After 24 hours, we remove the autoclave from the apparatus and allow it to be cooled. Then transfer the solution to another container and this time it should be precipitated using a centrifuge. The solution is centrifuged several times, and then washed with deionized water over several steps to remove any impurities. Now put the final solution in the oven at 50 °C for one day to be dried. Now the desired complex is ready to be analyzed and investigated.

CdTe synthesis

Hydrazine was first dissolved in a vessel containing 100 ml of water and after a short period of time, tellurium chloride was added to it. Then the solution was placed on a magnetic stirrer for 1 hour to every material be dissolved well. Then the ammonia was dissolved separately in another container containing 100 ml of water and then cadmium nitrate was added to it, then placed on a magnetic stirrer for 1 hour to be dissolved well. After one hour, we mixed both solutions into a three-spout balloon, and while one of the spouts is closed, nitrogen gas is added to the solution from the other two spouts. We transfer the solution into the autoclave after 4 hours. Then we placed the autoclave into an oven at 180 °C for 5 hours. After 5 hours, the apparatus was switched off and the autoclave was removed and the solution was transferred to another container after being cooled, then it subjected to centrifuge to remove the precipitate and was washed several times with deionized water. Finally, the precipitate was placed at 50 °C for 1 day to be dried.

Synthesis of CdTe complex with Znq_2

To synthesize this complex, we repeat the process of synthesizing CdSe complex. This time, we use CdTe quantum dot synthesized above and green synthesized Znq_2.

To do this, first the CdTe quantum dot was dissolved in a vessel containing 100 ml of water, then Znq_2 was dissolved in another vessel containing 100 ml of water. After 1 hour, both solutions were mixed and placed on magnetic stirrer for 1 hour. Then the prepared solution was transferred to the autoclave and placed in the oven for 24 hours at 150 °C. After 24 hours we remove the autoclave and allow it to be cooled. Then transfer the solution to another container and this time it should be precipitated using a centrifuge. The solution was centrifuged several times, and then washed with deionized water over several steps to remove any impurities. Then put the final solution into the oven at 50 °C for one day to be dried.

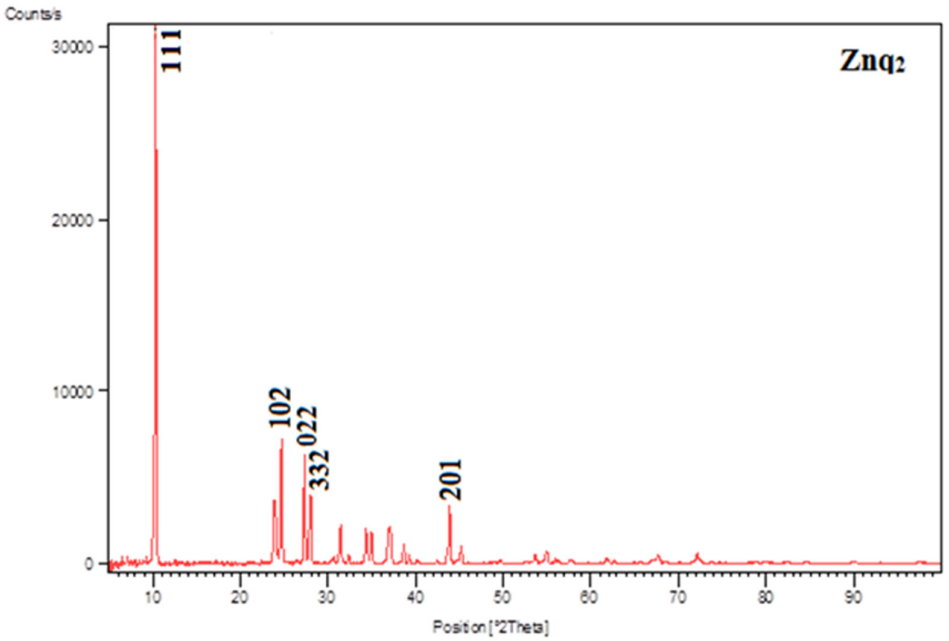


Fig. 1. XRD pattern of Znq_2

RESULTS AND DISCUSSION

After completing the above steps and preparing the final complex, we now need to perform the necessary analyzes to investigate the results of the research. In this study, we analyzed the product in terms of structural, behavioral, morphological, as well as optical properties. Then we analyzed the data collected. The structural behavior of the complex was investigated by XRD, its morphology by SEM, its optical behavior by Uv-visible transition spectrum and photoluminescence.

At this stage, the quantum dot structure and its final complexes were investigated under XRD analysis using X-ray device made by Philips company having λ= 2.289 Angstrom Model X'pert MPD PRO-pw3040 / 60. The obtained data were in the range of 2θ from 10 to -90. According to the Figures, Znq_2 spectral pattern has three main peaks at 2θ of -10^0-25^0-27^0-28^0 which almost corresponded with the reported results, and its average crystallite size is 2nm (Fig. 1). The main peaks of CdSe are at 2θ of -10˚-24˚-44˚ which corresponds to the reported results, and its average crystallite size in this spectrum, calculated using the Shearer equation, is 3.2788 nm (Fig. 2) [16-17].

The main peaks of CdSe complex are also at 2θ of -10˚-24˚-43˚ and the average crystallite size in this spectrum is 1.6967 nm. The CdTe quantum dot spectrum has three main peaks at 2θ of 33˚-35˚-41˚ that almost corresponds to the results mentioned and the average crystallite size is 2 nm (Fig. 3). The CdTe complex spectrum also has three main peaks at 2θ of -27˚-25˚-10˚ and the average crystallite size is 2 nm. The following images are correspond to the spectra listed in the order above.

The structure and final size of the product were also investigated by SEM analysis, where the final complexes were analyzed here. Fig. 4 shows the CdSe complex and Fig. 5 shows CdTe complex, both with different magnifications.

In Fig. 4, images are obtained on a scale of 2 µm, 200 , with image 1 having the magnification of 10000, and image 2 having the magnification of 100000. According to the images, the average size of the nanoparticles is 152 nm. According to EDX analysis, it can be said that the skein (or cabbage) shapes are CdSe quantum dots which have been green synthesized on Znq_2 sheets.

Fig. 5 also illustrates images on a scale of 1 µm and 500 nm with image 1 having the magnification of 30000, image 2 having the magnification of 50000 times. According to the images, the average size of the nanoparticles is 152 nm. According to EDX analysis, it is estimated that the fine grains correspond to the CdTe quantum dots and the plate shapes correspond to Znq_2.

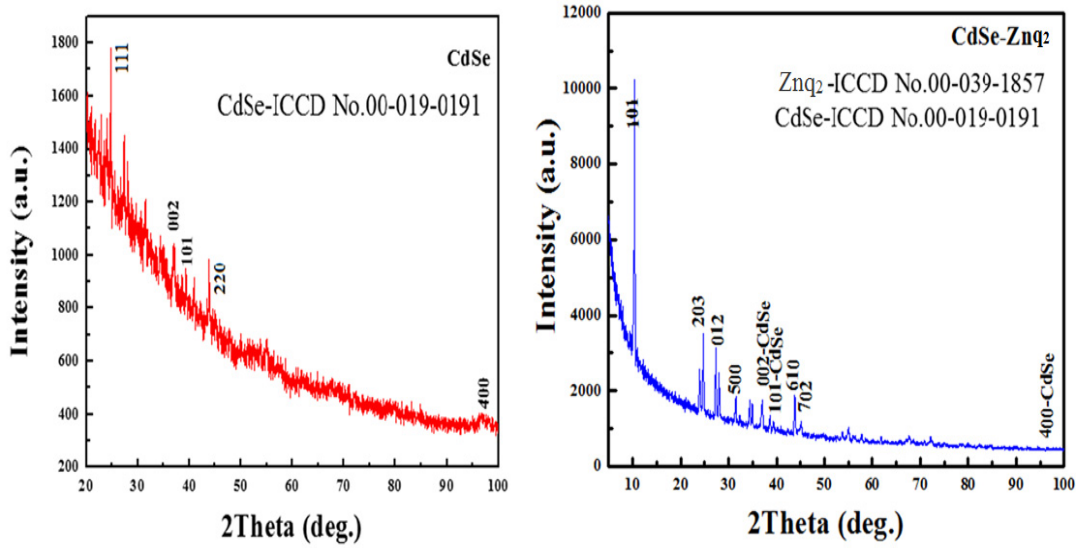


Fig. 2. XRD patterns of CdSe and CdSe-Znq_2

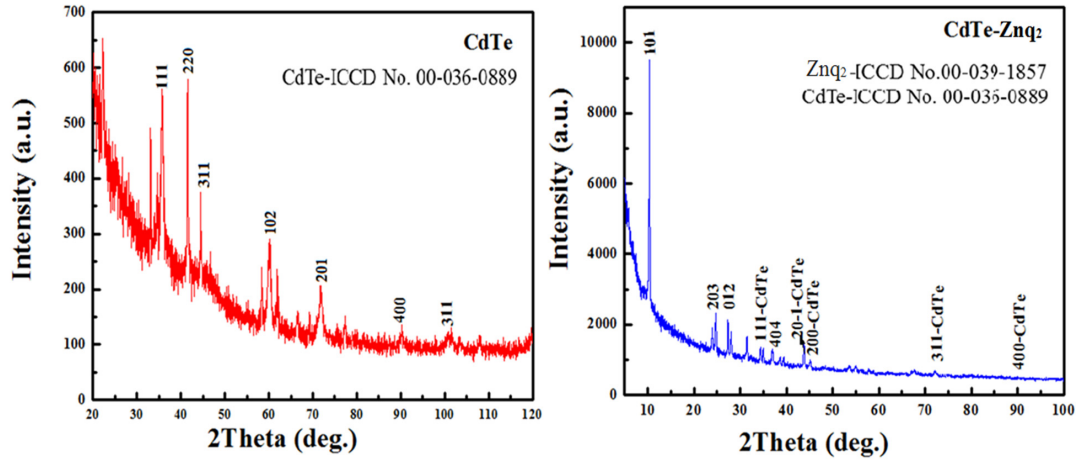


Fig. 3. XRD patterns of CdTe and CdTe-Znq_2

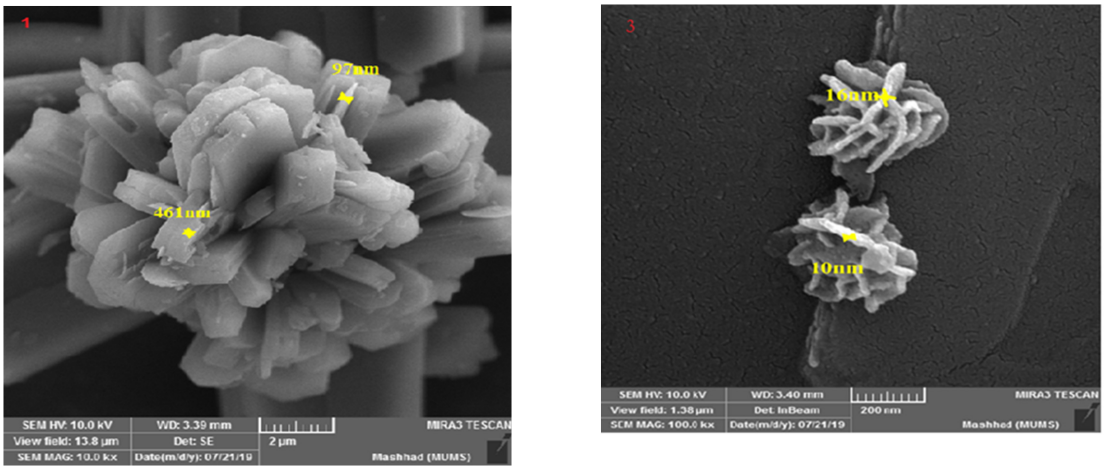


Fig. 4. SEM images of CdSe –Znq_2 (1) MAG:10Kx, (2) MAG: 100Kx

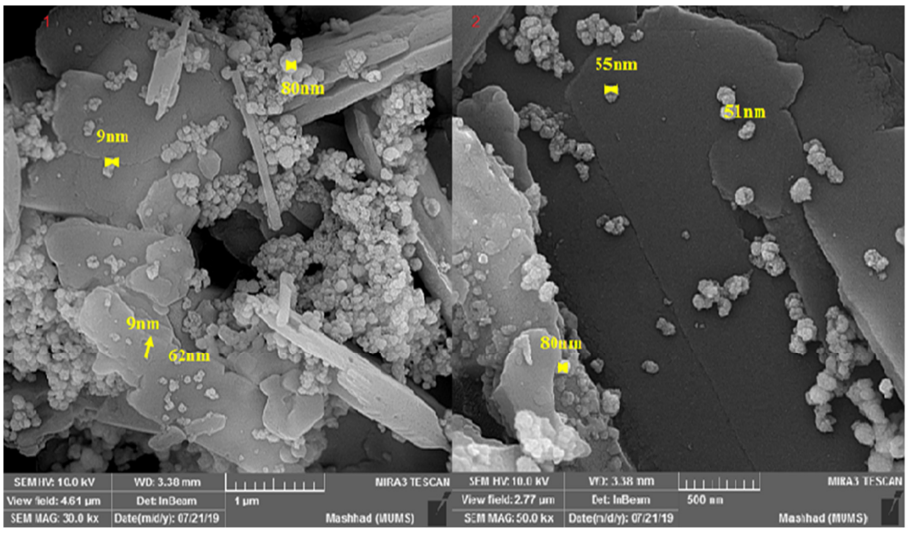
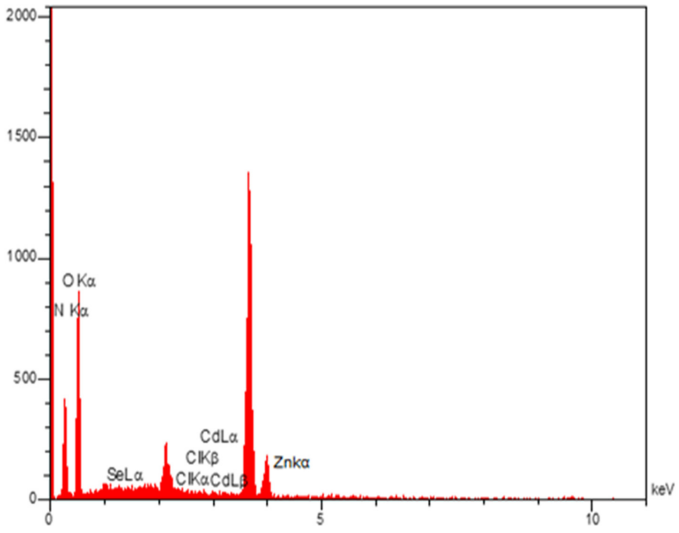


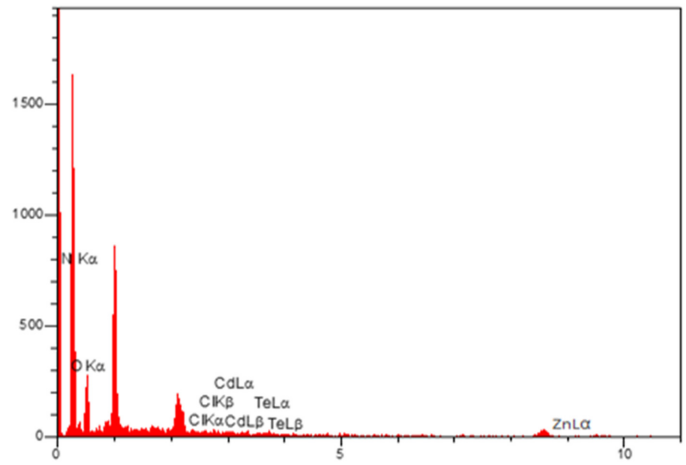
Fig. 5. SEM images of CdTe-Znq_2 (1) with MAG:30Kx, and (2) MAG:50Kx



Elt	W%	A%
N	7.92	9.87
O	81.15	81.13
Cl	0.74	0.49
Se	6.43	5.86
Cd	1.09	0.89
Zn	2.67	1.76

Elt	W%	A%
N	8.87	10.40
O	84.49	88.18
Cl	0.43	0.20
Se	2.71	0.56
Cd	1.62	0.24
Zn	1.48	0.42

Fig. 6. EDX spectrum of CdSe complex



Elt	W%	A%
N	6.51	7.73
O	79.27	79.02
Cl	o.87	0.43
Cd	1.78	0.84
Te	8.33	8.12
Zn	3.24	3.86

Elt	W%	A%
N	25.75	28.79
O	70.65	70.68
Cl	0.24	0.11
Cd	0.78	0.11
Te	1.38	0.17
Zn	1.2	0.14

Fig. 7. EDX spectrum of CdTe complex

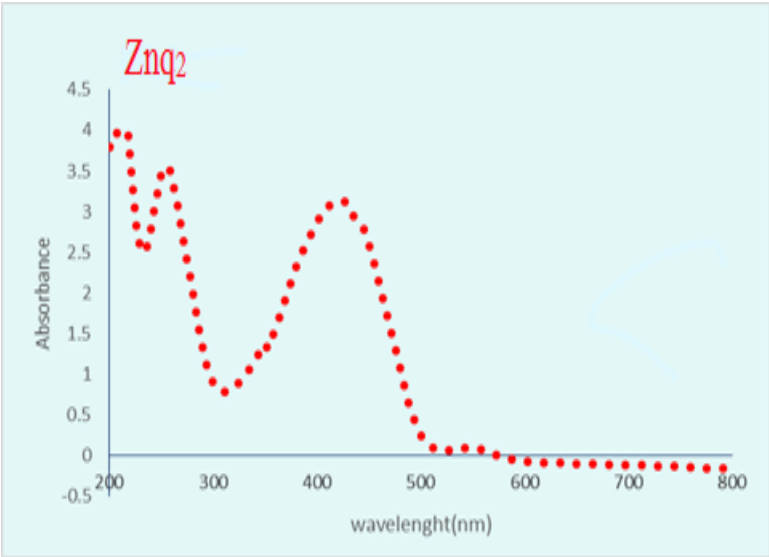


Fig. 8. Znq_2 absorption spectrum

Energy dispersive X-ray spectroscopy EDX is applied for structural analysis or identifies sample chemical properties. The final complexes of our study were also subjected to X-ray spectroscopy. The following Figure shows the CdSe and CdTe complexes spectroscopy results.

The final products were subjected to UV-Visible and PL analysis to be investigated optically. The absorption spectrum was taken to detect the internal vibrations of the synthesized particles, as well as photoluminescence spectrum was taken from them to investigate their luminescence. Fig. 8 shows the absorption spectrum of Znq_2 that has 3 absorption peaks at 220, 260 and 430 nm.

In Fig. 9, the absorption spectra of CdSe quantum dot and its complex are compared. As we can see from the Figure, the CdSe quantum dot has only one absorption peak at 224 nm and its complex has a strong absorption peak at 225 nm as well as a weak absorption peak at 260 nm. And In Fig. 10, the absorption spectra of the CdTe quantum dot and its complex are compared, and

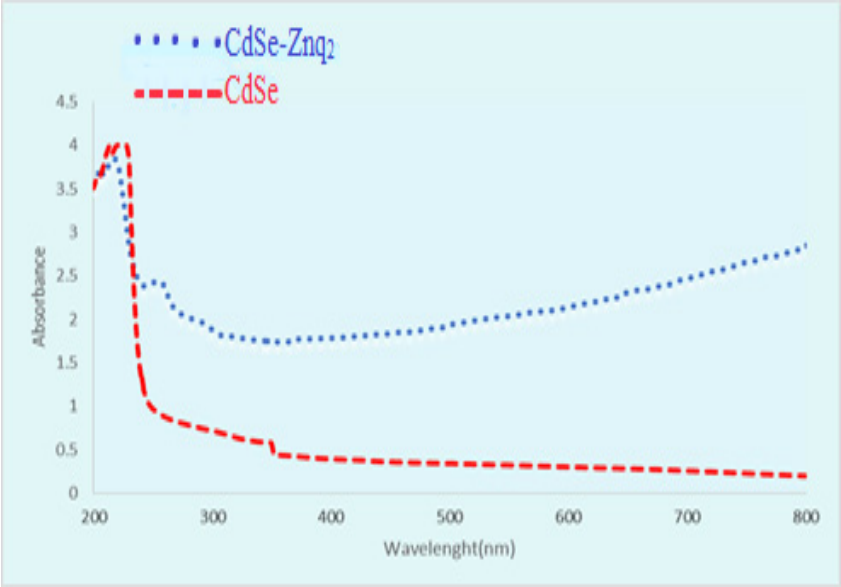


Fig. 9. Comparison of the absorption spectra of CdSe and CdSe-Znq_2

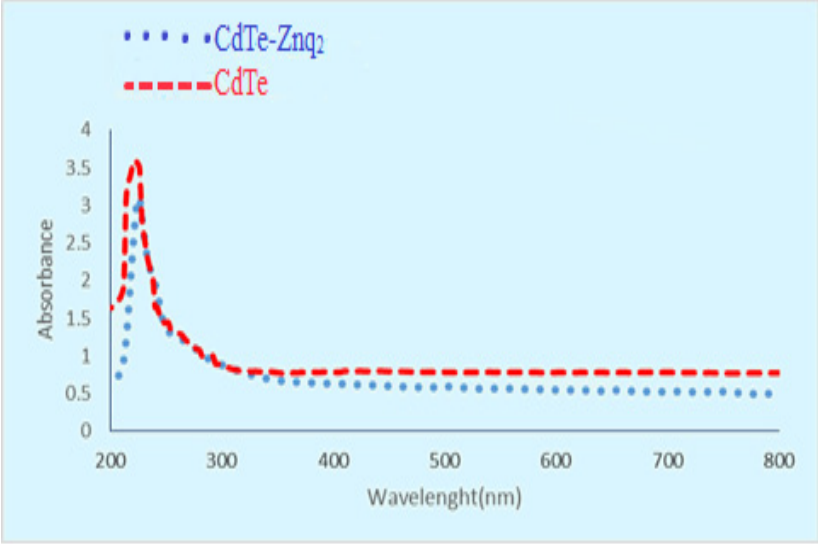


Fig. 10. Comparison of the absorption spectra of CdTe and CdTe-Znq_2

both have a strong absorption peak at 225 nm.

Fig. 11 shows the photoluminescence spectrum of Znq_2. We see from the pattern that it has a strong propagation peak in the range of 400 to 600 nm. In Fig. 12, the photoluminescence spectra of CdSe quantum dot and its complex are compared. According to the figure, both have a propagation peak at 520 nm. Also the CdSe complex has a weak propagation peak at 380 nm. In Fig. 13, the photoluminescence spectra of CdTe quantum dot

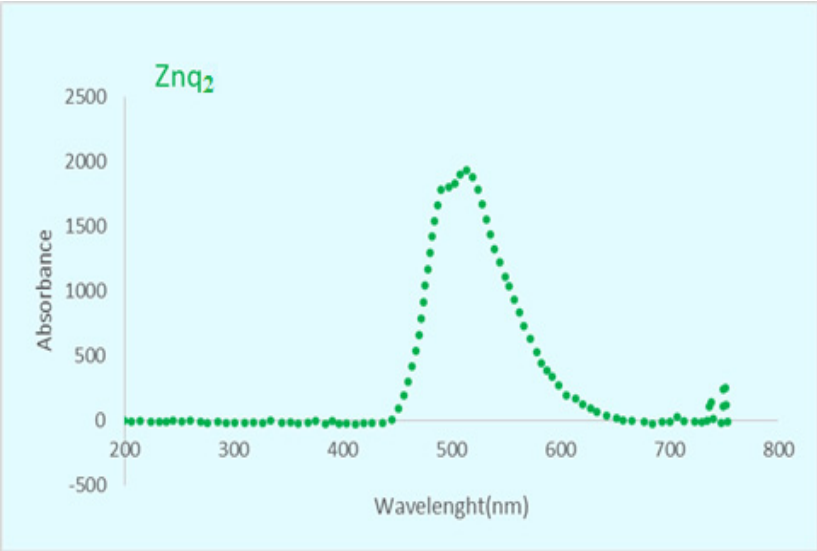


Fig. 11. PL emission spectrum of the Znq_2 nanoparticles

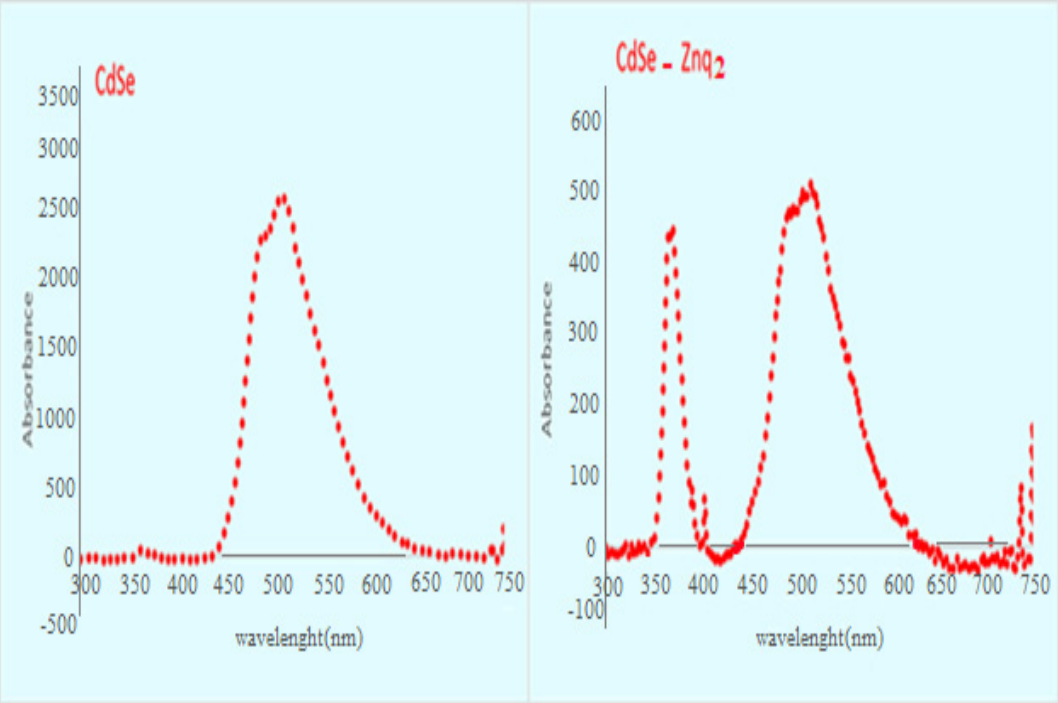


Fig. 12. PL comparison of the CdSe quantum dot spectrum and CdSe-Znq_2

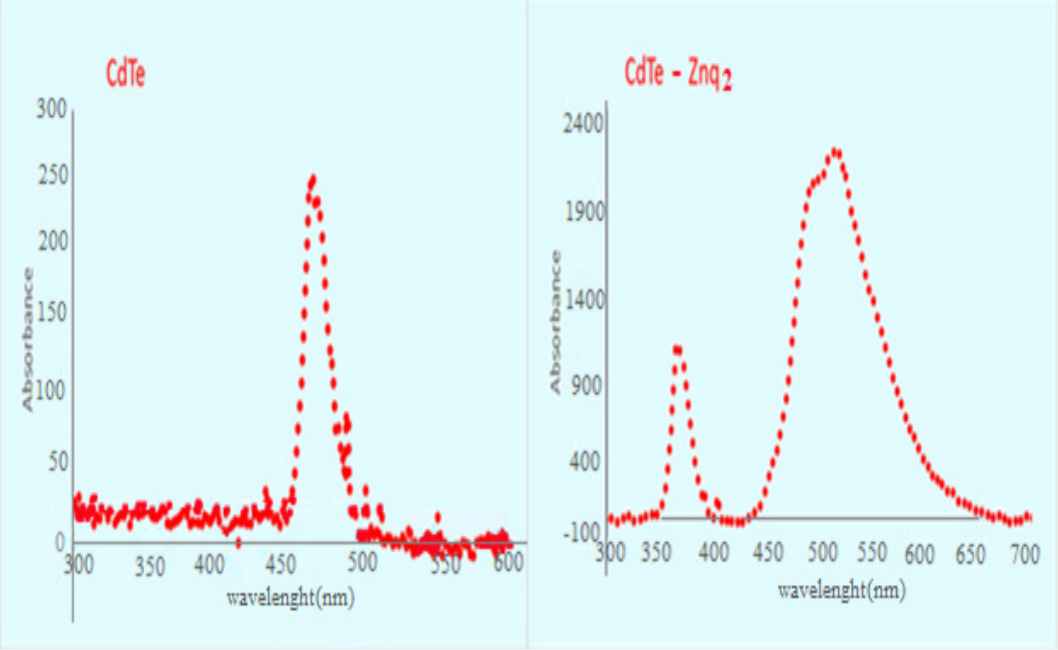


Fig. 13. PL comparison of the CdTe quantum dot spectrum and CdTe-Znq_2

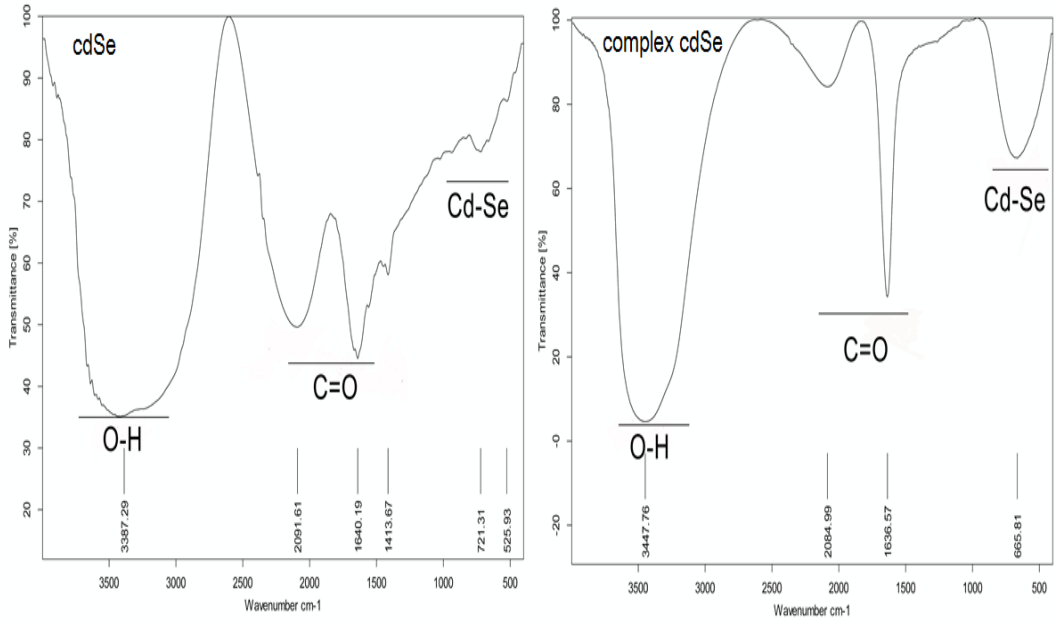


Fig. 14. FT-IR spectra of the CdSe quantum dot and its complex

and its complex are compared. According to the figure, CdTe complex has two propagation peaks at 510 and 370 nm, but CdTe spectrum pattern has only one propagation peak in the range of 450 to 500 nm [21-26].

To find the bonds of the functional groups formed in the synthesized products, the spectra obtained from FT-IR analysis were investigated. As you can see from the Figure, the spectrum is ranging from 500 to 4000 cm^{-1}. As the Figures show, in the range of 500 to 1000 cm^{-1} the vibrations are belong to the quantum dots and cadmium bonds,

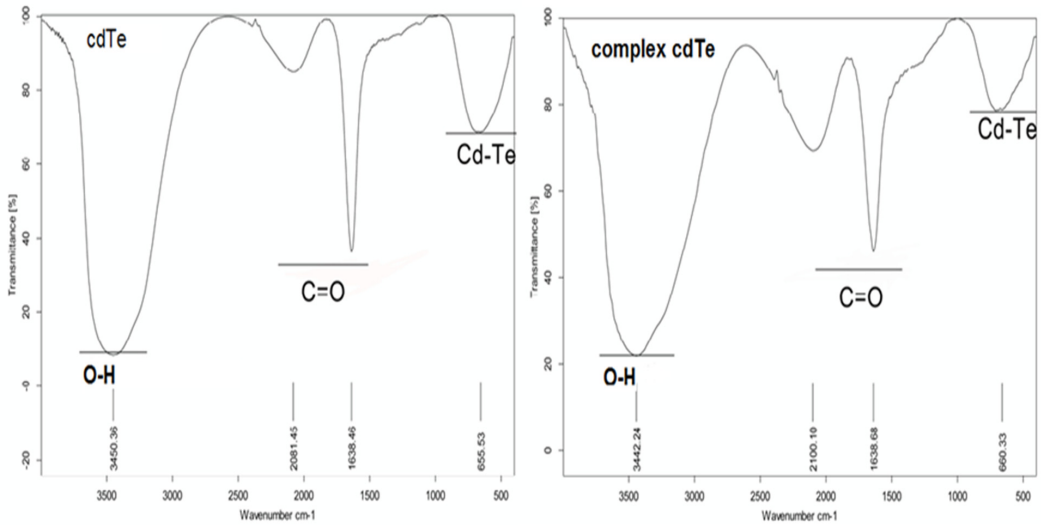


Fig. 15. FT-IR spectra of the CdTe quantum dot and its complex

i.e. cd-Se and cd-Te. In the range of 1500 to 2500 cm^{-1} the tensile vibrations of the C=O bonds are observed. Peaks in the range of 3000 to 3500 cm^{-1} represent vibrational bands corresponding to the O-H bond.

CONCLUSION

In this study, we first synthesized the quantum dots and then investigated their effects on the green synthesized metal complex Znq_2. The results show that upon compositing these nanostructures, their luminescence properties remained intact. So, we can use these nanostructures in organic light emitting diodes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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