ISSN: 0067-2904

Study the Structure Properties of CdTe and CdTe/CdSe Quantum Dots at pH=12 using an Aqueous Method

Husham. N. Noori*, Ameer F. Abdulameer
Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

Received: 28/6/2022 Accepted: 25/12/2022 Published: 29/2/2024

Abstract

This research aims to study the structural properties of cadmium telluride (CdTe) core QDs and cadmium telluride/ cadmium selenium (CdTe/CdSe) core-shell QDs at pH 12. The QDs were prepared using aqueous synthesis by reflux process. The structural properties of the QDs were studied using X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray spectroscopy (EDX), and Transmission Electron Microscopy (TEM). The results of the XRD analysis for CdTe QDs and CdTe/CdSe QDs showed that they have three diffraction peaks in the directions (111), (220), and (331) with a slight shift in the diffraction peaks of CdTe/CdSe QDs, which indicates the successful packing of selenium atoms around CdTe. FESEM results confirmed that CdTe and CdTe/CdSe QDs possess quantum spherical NPs with diameters ranging from 27 nm to 41 nm. The EDX results confirm corrections of added concentrations The histogram images of the TEM analysis show that the diameters of CdTe and CdTe/CdSe are 7nm and 9 nm, respectively.

Keywords: Refluxing method, aqueous method, XRD, TEM, FESEM.

دراسة الخصائص التركيبية للنقاط الكمومية *CdTe* و *CdTe / CdSe* عند *PH = 12* بأستخدام الطريقة المائيه.

هشام نصير*, أمير فيصل عبد الآمير
جامعة بغداد , كلية العلوم , قسم الفيزياء, بغداد, العراق

الخلاصة:

يهدف هذا البحث إلى دراسة الخصائص التركيبية للنقاط الكمومية كادميوم تلورايت (CdTe) و كادميوم تلورايت/ كادميوم سيلينيوم (CdTe/CdSe) لب قشرة عند درجة الحموضة 12. تم تحضير النقاط الكمومية باستخدام التخليق المائي من خلال عملية الارتداد. تمت دراسة الخصائص الهيكلية للنقاط الكمومية باستخدام حيود الأشعة السينية (XRD) ، والمسح المجهري الإلكتروني (FESEM) ، والتحليل الطيفي للأشعة السينية المشتتة للطاقة (EDX) ، والمجهر الإلكتروني للإرسال (TEM). أظهرت نتائج تحليل XRD لـ CdTe QDs و CdTe / CdSe QDs أن لديهم ثلاث قمم حيود في الاتجاهات (111) و (220) و (331) مع تحول طفيف في قمم الحيود لـ CdTe / CdSe QDs ، مما يشير إلى التعبئة الناجحة لذرات السيلينيوم حول CdTe. أكدت نتائج FE–SEM أن النقاط الكمومية CdTe و CdTe / CdSe تمتلك جسيمات نانوية كروية كمومية

*Email: hushamnassernoori@gmail.com

بأقطار تتراوح من 27 نانو إلى 41 نانو. أكدت نتائج EDX التراكيز المضافة. تظهر النتائج الموضحة في الرسوم البيانية لـ TEM أن أقطار CdTe و CdTe / CdSe هي 7 نانومتر و 9 نانومتر ، على التوالي.

1. Introduction:

Nanomaterials (NMs) are vast groups of atoms, up to billions, combined to form a ball whose diameter does not exceed a few nanometers. NMs are prepared in several ways depending on the desired application. NMs and NPs have a very large surface area compared to their volume [1]. This feature gives the NPs unique electrical and optical properties that differ from their bulk materials. These properties are obtained by controlling the nanoparticles size to suit the required applications. The process by which electrons are confined to a specific space is called quantum confinement [2]. The quantum confinement effect on the structural and optical properties begins when the particle size becomes smaller than the electron's wavelength [3]. Quantum dots (QDs) are NPs in which electrons are constrained from moving in three dimensions [4]. Despite their unique properties, these NPs are characterized by low stability due to oxidation and agglomerations that reduce their effectiveness in the outer environment. Therefore, a study or a new technique was directed that enabled researchers to retain the properties of these materials by encapsulating the NPs. The final product is called a core shell when the nanoparticle is encapsulated in a shell [5]. It is defined as a nanoparticle of a semiconductor material encapsulated by a semiconductor nanomaterial, CdSe/ZnS, CdTe/CdSe, are examples of such materials [6, 7], such that the energy gap of the core is less than that of the shell. This is to prevent electrons' leakage, control the core's size (i.e., prevent it from growing undesirably), and prevent the core from oxidation and corrosion that could affect its effectiveness and stability in the surroundings. Cadmium telluride (CdTe) and cadmium selenide (CdSe) are members of the II-VI group, which have been employed in various fields with the progress of scientific development in recent years due to their different properties from CdSe and CdTe bulk [8]. Cadmium telluride (CdTe) is direct-gap, of approximately 1.53 eV, semiconductor [9]. Cadmium-selenium (CdSe) is one of the most popular in semiconductors applications, with a direct energy gap of about 1.74 eV [10]. CdTe and CdSe are prepared using various syntheses such as ultrasonic [11], thermal [12], organic [13], and aqueous [14]. The aqueous synthesis method is the most popular of the various syntheses, as it is an inexpensive, environmentally friendly method that provides good compatibility between nanoparticles and biological [15, 16].

2. Experimental and Aim of Work:-

Cadmium acetate dihydrate (Cd (Ac_2) .$2H_2O$) was used as a source of cadmium (Cd) using a liquid consisting of a 3-mercaptopropionic acid (3MPA) matrix to arrange the atoms. Potassium tellurite ($KeTeO_3$) was used as a source of trihydrate Te and sodium brohydrate ($NaBH_4$) worked on reducing Te to Te^{-2} and stopping its diffusion. Sodium sulfate (Na_2SeSO_3) ions were used as a source of Selenium (Se). Sodium hydroxide (NaOH) was used to adjust the acidity to obtain the required particle size. This research aims to study the structural properties of the CdTe QDs and CdTe/CdSe core-shell QDs at pH=12.

2.1 Chemical Materials

The materials used were $KeTeO_3$ (95%) (From India), NaOH (from India), Cd(Ac_2).$2H_2O$ (95%) (Merck KGaA, Germany), 3-MPA (99%) (From Sigma Aldrich), $NaBH_4$ (95%) (Alpha Chemika, India), and deionized water (D.W.). All materials were used without purification.

2.2 Preparation Method

CdTe QDs and CdTe/CdSe QDs were prepared following the same approach of Ncapayi et al. [15] using an aqueous method at pH=12 [17], but with a difference in the volume of Se solution added to the CdTe QDs solution to prepare CdTe/CdSe QDs. QDs were prepared using a stirrer at a speed of 400 rpm instead of an oil bath, using the refluxing method for 7h and at a temperature of 100^0C, inside a 250ml three-neck flask. Se was prepared in the laboratory using the same approach as Ncapayi et al. [15] but with different temperatures and times. A solution of Se was prepared by dissolving (4mmol) 0.503g of sodium sulfate (Na_2SO_3) in 50ml of deionized water in a 100ml three-neck flask and left for about 5 minutes under stirring at a speed of 400 rpm to obtain complete dissolution. After that, the temperature of the solution was raised to 70^0C for half an hour. Then (2mmol) 0.15793g of selenium was added to the solution, and the temperature was raised to 90°C for three hours. The prepared Se solution was kept away from light and used on the second day, noting the presence of residues of selenium sediment at the bottom of the beaker.

CdTe/CdSe QDs were prepared by adding 5ml of Se into a hot solution of another reflux process of CdTe QDs after 1h of refluxing at 100^0C. The reaction was stopped by adding ethanol. After that, the solution was separated by centrifuge at 5000 rpm for 30 min. A red precipitate was obtained, which was then washed with ethanol and D.W at a ratio of 6:1. The solution was filtered using filter paper. The QDs powder was formed after 2h of heating the wet powder in the oven at 60°C. Finally, a certain amount of the powder was taken to be re-dissolved to examine its structural and topographical properties on a glass substrate. The washing process of the glass substrates followed the same steps as in our previous research [19].

3. Results and discussion

3.1 X-Ray diffraction

Figure (1) Shows the XRD patterns of CdTe QDs, CdTe/CdSe CS QDs powder. The patterns showed the distinct peaks of the CdTe at angles $2\theta= 25.085^0$, 42.545^0, and 49.571^0 due to (111), (220), and (331) Millar indices levels, respectively, and it matches the data of cart (JCPDS no. 65-1046) values. This result confirmed the cubic zinc blend structure of CdTe QDs. The absence of Miller's coefficients (102) and (103) at angles $2\theta = 33^0$ and 43^0 is the best evidence for the absence of a hexagonal wurtzite CdTe QDs and that the composition is pure cubic zinc blended structure [20, 21]. This is due to the temperature in the preparation process, where the second composition is present at high temperatures (above 260^0C) compared to the first composition, which is more stable at low temperatures [22]. While CdTe/CdSe CS QDs XRD pattern showed diffraction peaks at $2\theta= 25.248^0$, 41.995^0, 49.744^0.

After the first shell growth, CdSe is around the CdTe core. A shift was observed in the diffraction angles toward higher angles values also noted is the widening and intensity increase of the diffraction peaks, confirming the growth of the NPs shell around the core. This result is in agreement with that of Sitrotin and Shaskolskaya [23].

FWHM, d-spacing, and grain size were calculated and stimulated using an X Pert High Score (ver. 2.1(1.1)) and compared with the standard values in (JCPDS no. 65-1046) for core, core-shell, and core-shell-shell powder, as listed in Table (1).

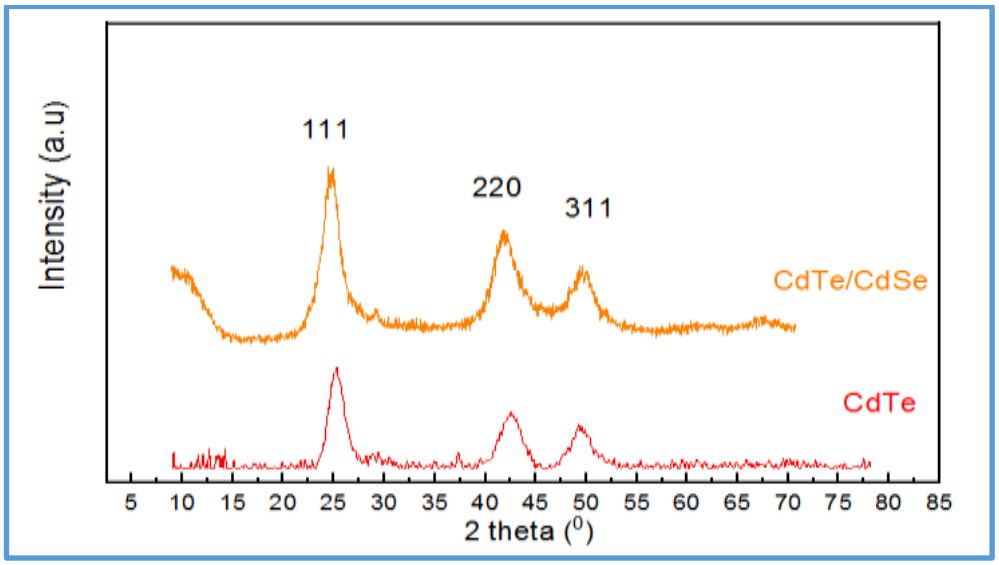

Figure 1: XRD spectra of *CdTe and CdTe/CdSe QDs* QDs capped with 3MPA.

Table 1: The calculated parameters from XRD spectra for QDs capping with 3MPA

$2\theta^0$ (Deg.)	hkl	d_{hkl} (nm)	FWHM (Deg.)	Grain Size (nm)	Crystallite size (nm)
25.085	111	3.547093	1.989	41	4.1
42.545	220	2.123185	2.426	35	3.5
49.571	311	1.83745	2.403	37	3.7
		3MPA CdTe/CdSe QDs			
$2\theta^0$ (Deg.)	hkl	d_{hkl} (nm)	FWHM (Deg.)	Grain Size (nm)	Crystallite size (nm)
25.248	111	3.524561	2.115	39	3.9
41.995	220	2.149711	3.079	28	2.8
49.744	311	1.831464	3.124	28	2.8

The grain size (G.S) of crystalline material can be calculated using the Scherrer equation [24]:

$$G.S = (k\,\lambda) / (\beta \cos \Theta) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1\text{-}2)$$

Where: G.S is the grain size, k is a constant equal to 0.9, β is the Full Width at Half Maximum measured in radian, and θ is the diffraction angle in (degree).

2. Field Emission Scanning Electron Microscopy (FESEM) of QDs.

The FESEM of as a synthesis 3MPA CdTe, and CdTe/CdSe QDs thin films, deposited by the drop casting method on a glass substrate are shown in Fig 2 at FESEM resolutions of 1 µm and 10 µm, and Fig 4 at resolutions of 100 nm and 200 nm. Figures 2 and 3 (a, b and c) show FESEM images characterized by white regions due to back scattered-electrons (BSEs) from elements with high atomic number, and black regions due to BSEs from elements low atomic number [25]. Figures 2 (a) and 3 (a) show FESEM images of CdTe nanocrystals (NCs). The nearly spherical NCs of CdTe became uniformly distributed over the entire surface. As can be seen, the nearly spherical shape NCs are agglomerates [26]. Figures 2 (b) and 3 (b) show FESEM image of the CdTe/CdSe core/shell. As can be seen, aggregated round particles of sizes below 45 nm are observed. Core/shell composed of CdTe and CdSe NPs exhibits different surface features. The core/shell has more pinholes and large particle aggregation [27].

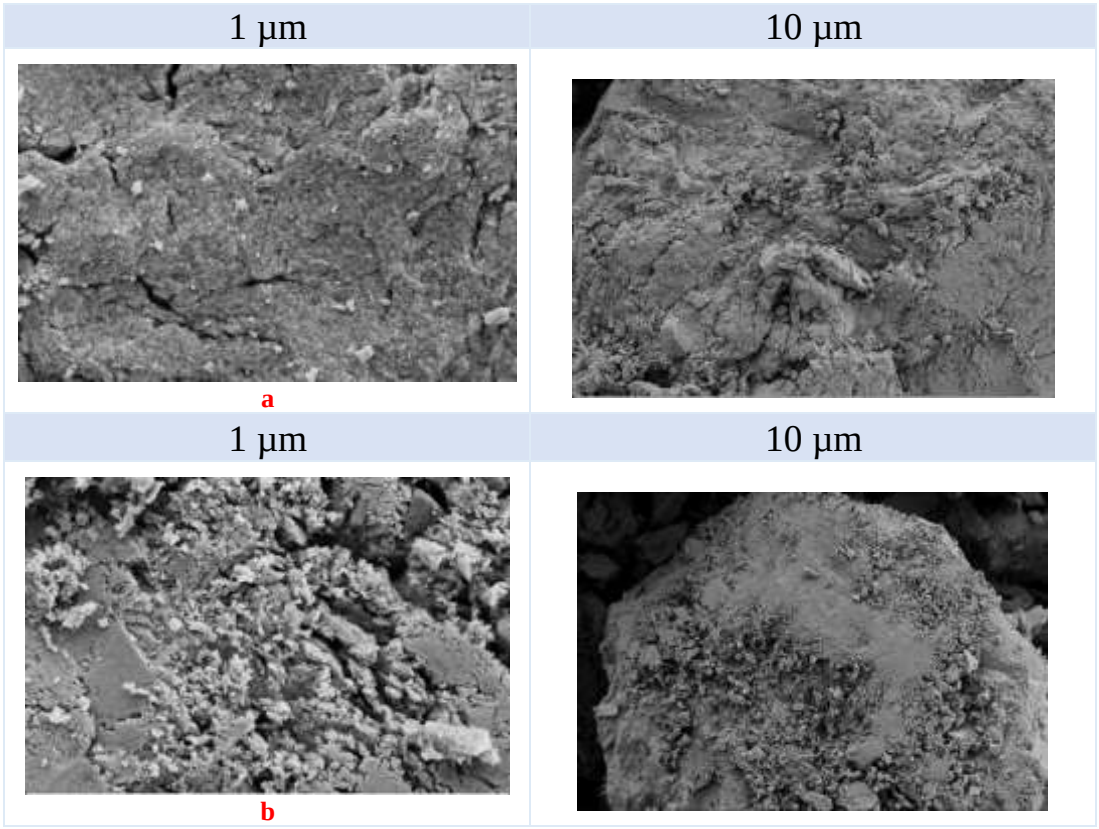

Figure 2: FESEM images of (a) CdTe, (b) CdTe/CdSe QDs for (1 µm) and (10 µm)

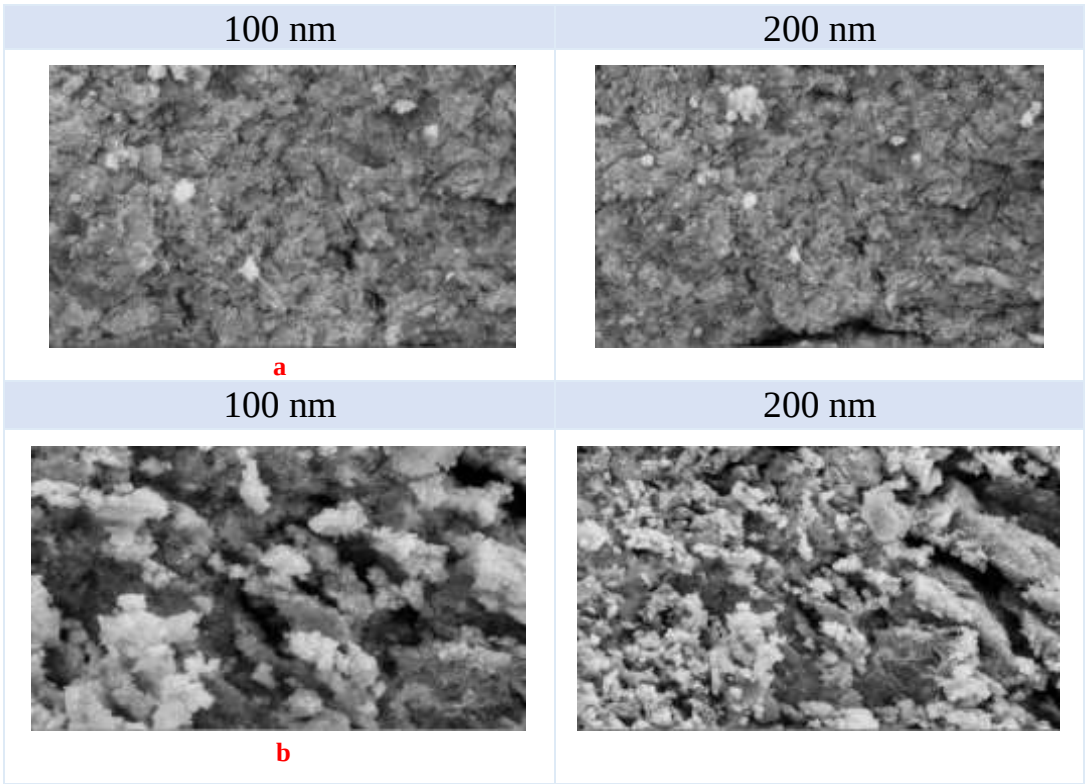

Figure 3: FESEM images of (a) CdTe, (b) CdTe/CdSe QDs for (100 nm) and ***(200 nm).***

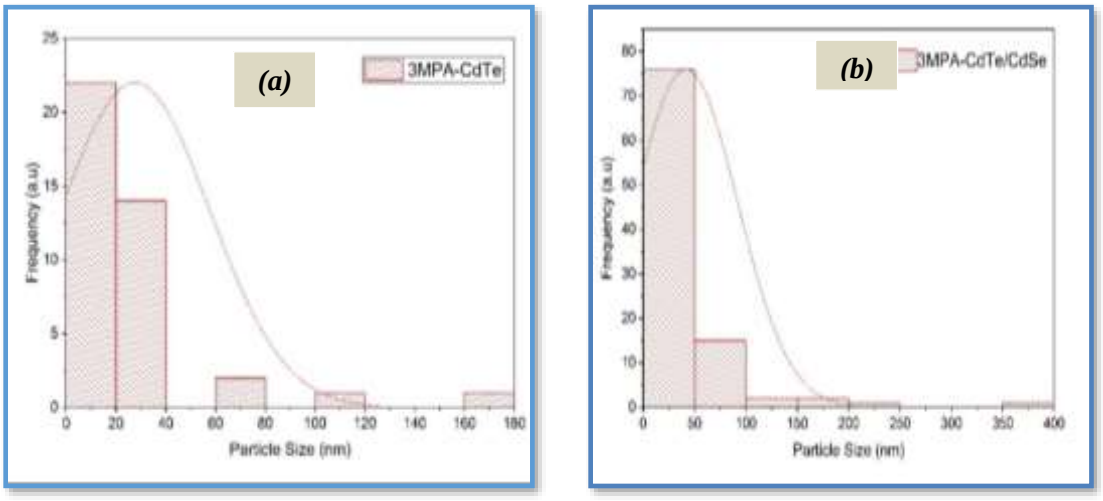

Figure 4: size distribution of (a) CdTe and (b) CdTe/CdSe QDs

3. Energy Dispersive X-ray (EDX) spectroscopy of QDs.

The EDX of as a synthesis 3MPA CdTe, and CdTe/CdSe QDs thin films, deposited by the drop casting method on glass substrate, are shown in Figures 5 (a and b), respectively. The EDX pattern confirms the nearly uniform presence of the Cd and Te elements, as shown in Figure 5 (a). From Figure 5 (b), the presence of the Cd, Te, and Se elements confirms the formation of the CdTe/CdSe core/shell. Each ratio of elements shown in the figures confirms corrections of added concentrations. Furthermore, it confirms the successful formation of core and core shell. These results are in agreement with those of Daramola et al. [27].

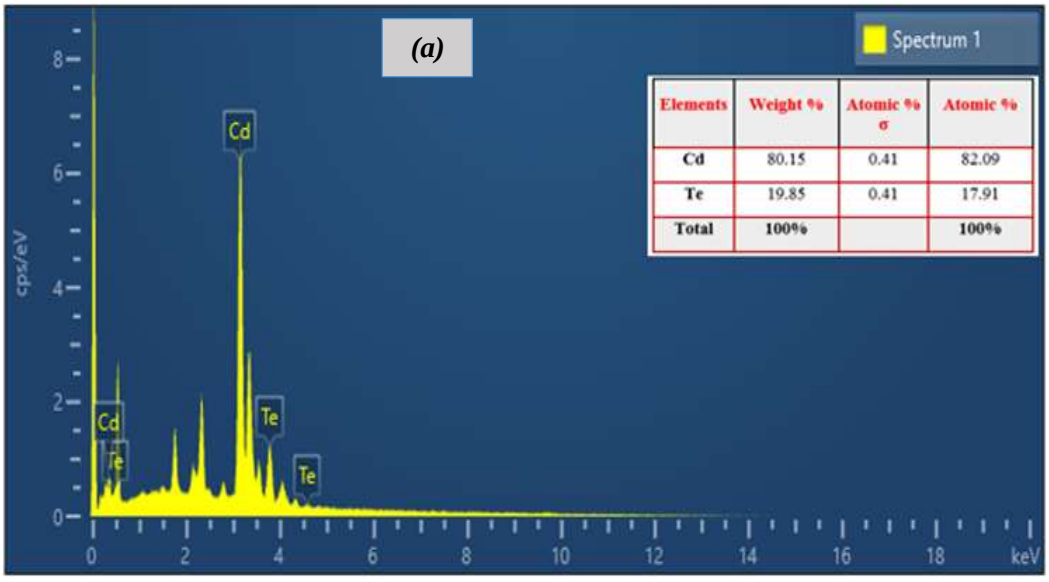

Figure 5a: FESEM images of (a) 3MPA CdTe, (b) 3MPA CdTe/CdSe QDs.

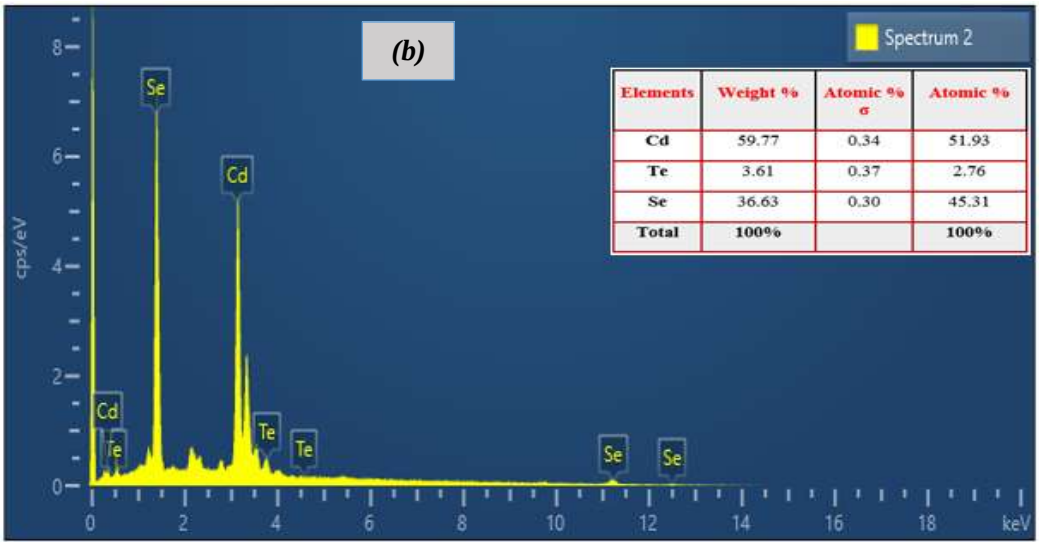

Figure 5b: FESEM images of (a) 3MPA CdTe, (b) 3MPA CdTe/CdSe QDs**.**

4. Transmission Electron Microscopy (TEM) of QDs.

The TEM of as a synthesis 3MPA CdTe QDs, CdTe/CdSe QDs solution are shown in Figure 6 (a) at scales 250 nm and 900 nm, and Figure 7 (b) at scales 30 nm and 80 nm. Figure 8 shows the histogram (size distribution) of QDs. TEM analysis was used to obtain the diameter value of particle size. Figures 6 (a and b) show that the morphology of the QDs exhibits a high density of monodispersed NPs which are of spherical shape. This increase in the size of the NPs is due to the additional coating around the core. This result is in agreement with that of Daramola et al. [27].

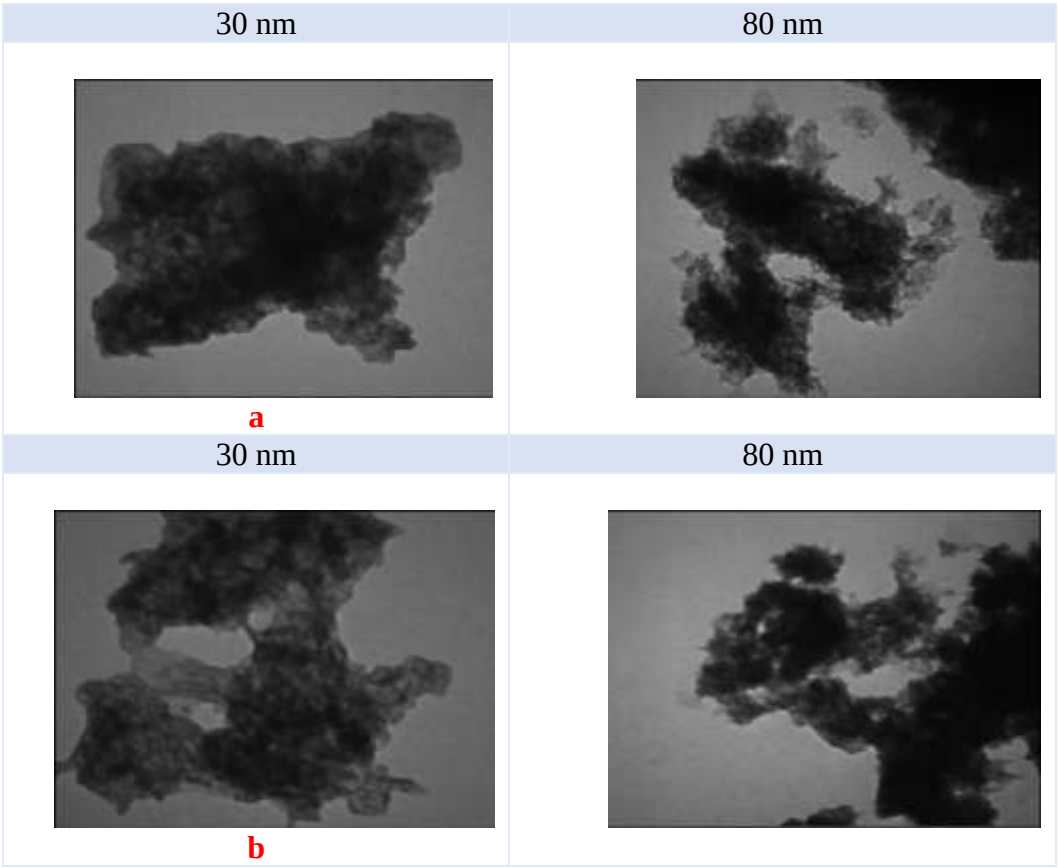

Figure 6: TEM images of (a) 3MPA CdTe QDs, (b) 3MPA CdTe/CdSe QDs

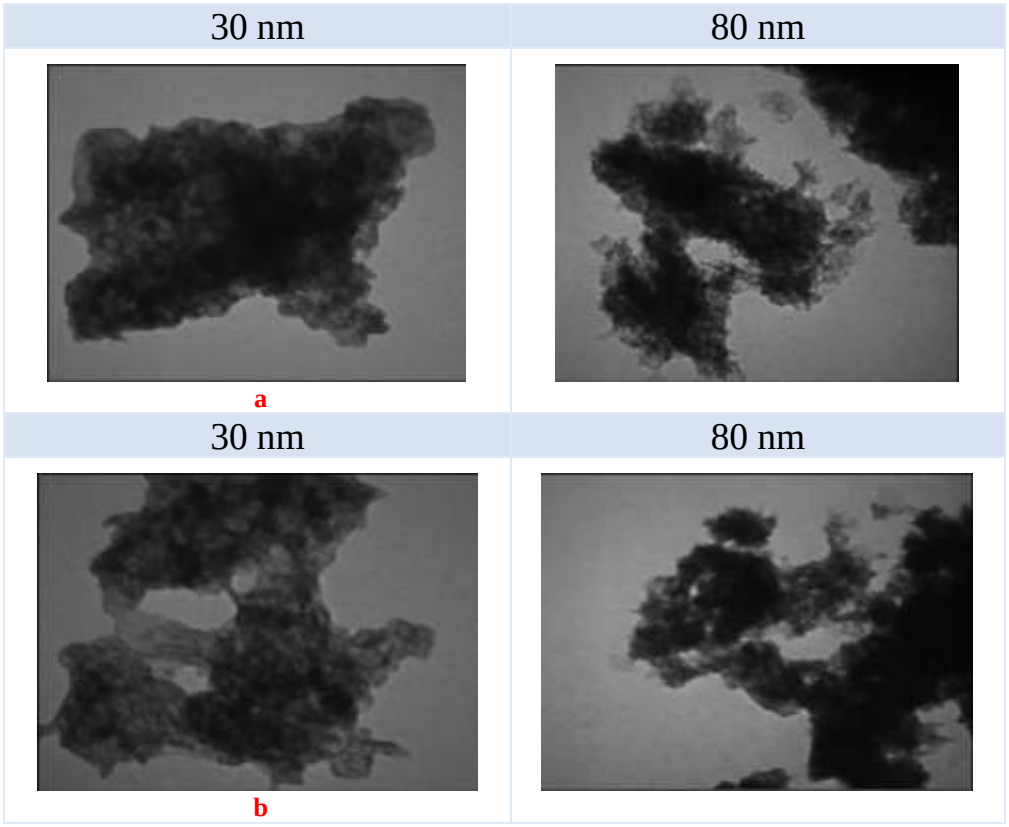

Figure 7a: TEM images of (a) 3MPA CdTe QDs, (b) 3MPA CdTe/CdSe QDs

The average NPs size calculated from Fig 8 was about 7nm and 9nm for CdTe and CdTe/CdSe QDs, respectively. The gradual increase in the average diameter of QDs emphasizes the effect of encapsulation on the diameter of the core, both core/shell and the core/shell/shell. The same results were found by Ahmed et al. [24].

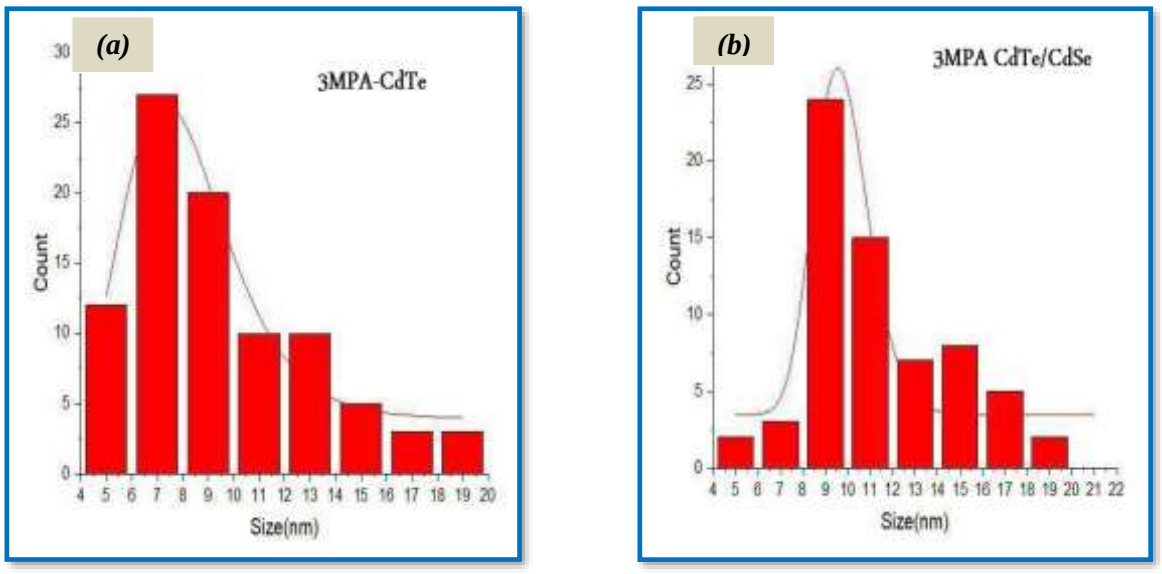

Figure 8: Histogram image of TEM showing the size distribution of (a) CdTe QDs, (b) CdTe/CdSe QDs.

The slight difference in the size values obtained by XRD and the TEM measurement can be explained by the fact that XRD analysis is used to measure the crystalline diameter. In contrast, TEM analysis measures the diameter of the core particles.

Conclusion

The results of the XRD analysis for CdTe QDs and CdTe/CdSe QDs showed that they have three diffraction peaks in the directions (111), (220), and (331) with a slight shift in the diffraction peaks of CdTe/CdSe QDs, which indicates the successful packing of selenium atoms around CdTe. FE-SEM results confirmed that CdTe and CdTe/CdSe QDs possess quantum spherical NPs with diameters ranging from 27 nm to 41 nm. The EDX results confirmed corrections of added concentrations. The histogram images of the TEM analysis showed that the diameters of CdTe and CdTe/CdSe were 7nm and 9 nm, respectively.

References

[1] F. Sabry, *Nanomaterials: The nanoparticles will be able to kill individual cancer cells, leaving the healthy ones alone: One Billion Knowledgeable*, 2022.

[2] C. Bhargava and A. Sachdeva, "*Nanotechnology: Advances and Real-Life Applications" CRC Press*, 2020.

[3] M. K. Jayaraj, "*Nanostructured Metal Oxides and Devices: Optical and Electrical Properties," Springer Singapore*, 2020.

[4] Schiffman J.D., Balakrishna R.G., "Quantum dots as fluorescent probes: Synthesis, surface chemistry, energy transfer mechanisms, and applications," *Sensors and Actuators B: Chemical*, vol. 258, p. 119, 2018

[5] M. Ray, "Synthesis of Core/Shell Nanoparticle." Lap Lambert Academic Publishing GmbH KG, 2013.

[6] S.P Raju, K. Hareesh, S. C. Pai, S. D. Dhole, G. Sanjeev, "Preparation of fluorescent CdTe@CdS core@shell quantum dots using chemical free gamma irradiation method", *Journal of Luminescence*, vol. 192, pp. 17-24, 2017.

[7] Y. Xie, Q. Tan, Z. Zhang, K. Lu, M. Li, W. Xu, et al., "Improving performance in CdTe/CdSe nanocrystals solar cells by using bulk nano-heterojunctions," *Journal of Materials Chemistry C*, vol. 4, pp. 6483-6491, 2016.

[8] M. Ando, H. Kawasaki, S. Tamura, Y. Haramoto, and Y. Shigeri, "Recent Advances in Gas Sensing Technology Using Non-Oxide II-VI Semiconductors CdS, CdSe, and CdTe," *Chemosensors*, vol. 10, no. 11, p. 482, 2022.

[9] J. M. Baruah, J. Narayan, "Surface passivated aqueous mediated synthesis of CdTe QDs: potential nano thin films," *Mater. Res. Express*, vol. 6, no. 9, P. 095082, 2019.

[10] Zubair M.S.H. Khan, Shamshad A. Khan, M. Zulfequar, "Study of thiol capped CdSe quantum dots using SeO_2 precursor for selenium source," *Mater. Sci. Semicond. Process*. vol. 57, pp. 190-196, 2017.

[11] F.D. Menezes, A. Galembeck, S. Alves Junior, "New methodology for obtaining CdTe quantum dots by using ultrasound,". *Ultrason. Sonochem*, vol. 18, no. 5, pp. 1008–1011, 2011.

[12] A. Kompany, B. Ghanbari Shohany, A. Khorsand Zak, "Characterization and optical properties of Cadmium Telluride nanopowders synthesized via hydrothermal method", *Journal of Research on Many-body Systems*, vol. 6, no.12, pp. 73-80, 2017.

[13] J.W. Kyobe, E. B.Mubofu, Y. M. M. Makame,S. Mlowe, N. Revaprasadu, "CdSe Quantum Dots Capped with Naturally Occurring Biobased Oils," *New J. Chem*. vol. 39, no. 9, pp.7251–7259, 2015.

[14] Y.L. Wang, S.Y. Liu, L. Y. Zhou, "An alternative aqueous synthetic route to preparing CdTe quantum dots with tunable photoluminescence," *Chin. Chem. Lett*., vol. 23, no. 3, pp. 359–362, 2012.

[15] V. Ncapayi, S. O. Oluwafemi, S.P. Songca, T. Kodama, "Optical and cytotoxicity properties of water soluble type II CdTe/CdSe nanoparticles synthesised via a green method,". *MRS Online Proceedings Library*. vol. 1748, pp. 69-75, 2015.

[16] Husham N Noori, Ameer F. Abdulameer, "A review of biosensors, definition, classification, properties, and applications," *Iraqi Journal of Science,* vol. 64, no. 11, pp 1-30. 2023.
[17] Husham N Noori, Ameer F. Abdulameer, "Study of the Effect of pH on the Optical Properties of the CdTe Quantum Dots,*" Iraqi Journal of Science,* vol. 64, no. 2, pp. 653-657, 2023.
[18] Husham N Noori, Ameer F. Abdulameer, "Study the optical and structural properties of CdTe Quantum Dots Capped with 3MPA Using Hydrothermal Method," *Chem. Methodol.,* vol. 6, no. 11, pp. 842-850, 2022.
[19] M. Xue, X. Wang, H. Wang, B. Tang, "The preparation of glutathione-capped CdTe quantum dots and their use in imaging of cells," *Talanta,* vol. 83, no. 5, pp. 1680–1686, 2011.
[20] W.W Yu, Y. A.Wang , X. G.Peng, "Formation and stability of size, shape-, and structure-controlled CdTe nanocrystals: ligand effects on monomers and nanocrystals," *Chem. Mater.,* vol. 15, no. 22, pp .4300–4308, 2003.
[21] R. M. Hodlur, M. K. Rabinal, "A new selenium precursor for the aqueous synthesis of luminescent CdSe quantum dots, " *Chem. Eng. J.,* vol. 244, pp. 82–88, 2014.
[22] Ganesh R. Bhand, Nandu B. Chaure, " Synthesis of CdTe, CdSe and CdTe/CdSe core/shell QDs from wet chemical colloidal method", *Materials Science in Semiconductor Processing,* vol. 68, pp. 279–287, 2017.
[23] Y. Sitrotin and M. Shaskolskaya, "Fundamental of crystal physics," Mir Publishers, Moscow, 1982.
[24] W. Ahmed, M. Booth, and E. Nourafkan, "Nanotechnologies for Renewable Energy: Elsevier Science," 2021.
[25] J. Du, C. Wang, X. Xu, Z. Wang, S. Xu, and Y. Cui, "Assembly of light-emitting diode based on hydrophilic CdTe quantum dots incorporating dehydrated silica gel," *Luminescence,* vol. 31, no. 2, pp. 419-422, 2016.
[26] M. Molaei, F. Farahmandzadeh, T. S. Mousavi, and M. Karimipour, "Photochemical synthesis, investigation of optical properties and photocatalytic activity of CdTe/CdSe core/shell quantum dots," *Materials Technology: Advanced Performance Materials*, vol. 37, no. 11, pp. 1818-1824, 2022.
[27] O. A. Daramola, X. Siwe-Noundou, P. F. Tseki, and R. W. M. Krause, "Rapid synthesis of thiol-co-capped-CdTe/CdSe/ZnSe core shell-shell nanoparticles: their optical and structural morphology," *Nanomaterials,* vol. 11, no. 5, p. 1193, 2021.