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Study of the Optical Properties of 3MPA CdTe and 3MPA CdTe/CdSe Quantum Dots at PH 12 in Different Periods of Time

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Abstract

This research aims to study the optical characteristics of semiconductor quantum dots (QDs) composed of CdTe and CdTe/CdSe core-shell structures. It utilizes the refluxed method to synthesize these nanoscale particles and aims to comprehend the growth process by monitoring their optical properties over varied periods of time and pH 12. Specifically, the optical evolution of these QDs is evaluated using photoluminescence (PL) and ultraviolet (UV) spectroscopy. For CdTe QDs, a consistent absorbance and peak intensity increase were observed across the spectrum over time. Conversely, CdTe/CdSe QDs displayed distinctive absorbance and peak intensity variations. These disparities might stem from irregularities in forming selenium (Se) layers around CdTe QDs during growth stages, which could potentially induce quenching in the emission spectrum. The optical examinations unveiled a discernible redshift towards higher wavelength values as the reaction progressed. This spectral shift was coupled with an enlargement in QDs size and a decrease in the energy gap. Using PL and UV analysis techniques enabled a comprehensive study of the optical attributes of the CdTe and CdTe/CdSe QD systems. Our findings underscored the influence of growth conditions and shell materials on the optical properties of QDs. The observed changes in absorbance, peak intensity, wavelength values, QDs size, and energy gap with increasing reaction time provided valuable insights into the growth dynamics of these QD structures.

Article Info.

Keywords:
Refluxing Method, Quantum Dots, Aqueous Method, pH, UV-vis.

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1. Introduction

Quantum dots (QDs) are defined as nanoparticles (NPs) in which the movement of electrons is restricted in all directions [1-4]. They have unique properties that differ from other nanoparticles with no quantum limitations. Nanomaterials (NMs) are a huge group of atoms, up to billions, combined to form a ball with a diameter of not more than a few nanometers [5]. They are prepared in several ways depending on the desired application and NMs have a very large surface area compared to volume [6]. For example, if a cube is divided, it will result in many cubes, each with a surface area, so if the cube is removed, it will result in a very large area. Also, its surface is water-repellent and has high activation energy since the bonds of surface atoms tend to be stable due to their lack of association with the outer surroundings, unlike the interior part of the material's surface [7]. Through tunning, it was possible to modify the properties of these materials based on the required application [8, 9]. This science is called nanotechnology due to the unique properties obtained [10]. In addition, semiconductors are used in various applications such as drug transport, biological applications, solar cells, and others [9-14]. Despite their unique properties, these nanoparticles have low stability due to oxidation and agglomerations that reduce their effectiveness in the external environment. Therefore, a new study or technique has enabled researchers to preserve the properties of these materials by encapsulating the nanoparticles. The final product is called a core-shell when the nanoparticle is covered with a shell. It can be defined as a nanoparticle from a semiconductor material coated with a semiconductor nanomaterial so that the energy gap of the core is less than that of the shell such as, CdTe/ZnS, CdTe/CdSe, and others [15-18].

Cadmium telluride (CdTe) is a semiconducting nanomaterial with a direct energy gap of approximately 1.53 eV. It is a good candidate for many applications, such as biological sensors, solar cells, and other applications [19-21]. On the other hand, Cadmium-selenium CdSe is one of the most widely used semiconductors with a direct energy gap of approximately 1.74 eV [22].

In this paper, CdTe was prepared using cadmium acetate dihydrate as a source of cadmium using a liquid consisted of a 3-mercaptopropionic acid 3MPA matrix to arrange the atoms [23-26]. $KeTeO_3$ is trihydrate Te and $NaBH_4$ is sodium brohydrate, work to reduce Te to Te^{-2} and stop its diffusion. Na_2SeSO_3 ions were released and prepared in the laboratory, and sodium hydroxide, NaOH, was used to adjust the acidity to obtain the required particle size [27, 28]. This research aims to study the optical properties of the growth of Core and Core-shell at PH=12 and different interval periods of time.

2. Experiment Work

2.1. Chemical Materials

The materials used are: $Cd(ACl_2).2H_2O$ (95%) (Merck KGaA, Germany), $KeTeO_3$ (95%) (India), sodium hydroxide (NaOH) (India), selenium (Se) (Merck KGaA, Germany), $NaBH_4$ (95%) (Alpha Chemika, India), 3-MPA (99%) (Sigma Aldrich), and deionized water (D.I). All materials were used without purification.

2.2. Preparation Method

CdTe and CdTe/CdSe QDs were synthesized using the method described in reference [29] at pH 12. The only difference was in the concentration of the Se solution used for coating CdTe QDs to form the CdTe/CdSe core-shell QDs. Additionally, a stirrer was employed at 400 rpm instead of an oil bath. The synthesis process involved the refluxing method at a temperature of 100 °C in a 250 ml three-neck flask. While for the core shell, the difference was in the volume of the Se solution added to the core solution as a shell around CdTe QDs. Also, Se was prepared in the laboratory, but with the difference in the time and temperature of the refluxed solution. Se was prepared by dissolving (4mmol) 0.503g of sodium sulfate (Na_2SO_3) in 50 ml of deionized water and then left for 5 min in a stirrer at a speed of about 400 rpm to obtain a homogeneous mixture. The temperature was raised to 70 ^{0}C for half an hour; after that, 0.15 g (2mmol) of Se was added to the solution, and the mixture's temperature was increased to 90 ^{0}C for 3 hrs. After completion, it was left for use the next day, noting precipitates of insoluble selenium at the bottom of the beaker. CdTe/CdSe was prepared by adding 5 ml of Se into a hot solution of another reflux process of CdTe QDs after 1 hr of refluxing at 100 ^{0}C. After the preparation process, a centrifugal device performed the complete separation process at a speed of 5000 rpm for 10 min. Finally, the remnants of unnecessary salts were removed by washing the QDs three times with a mixture of ethanol and deionized water (5:1) and put in an ultrasonic device to break up the insoluble particles to obtain a completely dissolved solution.

2.3. Tools

The tools used in this study are three-necks flask, beaker 100 ml, macro-dropper 1ml, goedkope pH meter, hot plate with a stirrer, condenser, magnetic bar, tube centrifuge, rubber stoppers, and thermometer.

2.4. Characterization Devices

The absorption spectra of the as-prepared CdTe QDs and CdTe/CdSe core shell QDs were characterized by UV-visible SP-8001 spectrophotometer and their corresponding PL spectra were measured using RF-1501 Spectro fluorophotometer (Shimadzu) under an excitation wavelength of 420 nm.

3. Results and Discussion

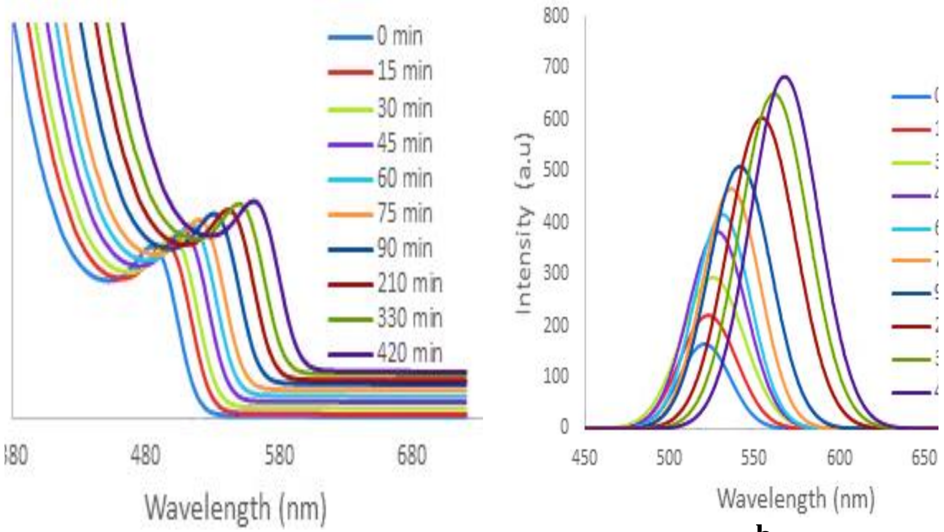
Fig. 1(a and b) shows the absorption and fluorescence spectra of CdTe QDs prepared at pH 12. Table 1 illustrates data obtained from the absorption and PL peaks for 3MPA-CdTe QDs. It was noticed in Fig. 1(a and b) that there is a regular increase in the values of the absorption and fluorescence spectra (shift from the blue region towards the red region or stock shift [30]), as well as an asymmetry increase in the intensity of the peaks with increasing reaction time. It can be attributed to NP's regular growth of nucleation or particle formation phase during their reaction periods [31-33]. The increase in the uniformity of the intensities of the fluorescence peaks can be attributed to the decrease of the precursor Cd^{+2} and Te^{-2} ions in the solution [34, 35], representing surface defects and a fluorescence inactivation factor [36, 37]. The values of the full width at half maximum (FWHM) are less than 50 nm during the interaction, indicating that CdTe QDs without surface defects, giving them good optical properties. Any increase in the FWHM values at the beginning of the reaction means irregularity in the NPs sizes during preparation [38-41].

Fig. 2 (a and b) shows the absorption and fluorescence spectra of CdTe/CdSe core-shell QDs prepared at pH 12. Table 1 illustrated data from the absorption and PL spectra peaks 3MPA-CdTe/CdSe QDs. It was noticed in Fig. 1(a and b) that there was a sudden shift in the absorption and PL spectrum towards the redshift when Se precursors were added to the solution after 90 min, which can be attributed to the formation of the CdSe shell towards CdTe [42-45]. The formation of the CdSe shell reduced the mobility of the charge carrier’s wave function, enhancing of quantum confinement effect (increase in energy gap) in the CdTe core. The energy gap in the CdTe core was lower than those in the CdSe shell. As a result, the CdTe QDs emit light at longer wavelengths (lower energies) or the shifting towards longer wavelength is a result of the energy transfer from higher energy CdTe QDs to the lower energy CdSe shell [46, 47]. Also, it can observe a decrease in the emission and PL intensities. This can be attributed to an increase in the NP's size and an excess of Se ions, which act as traps that form non-radioactive recombinants, decreasing the intensities of the fluorescence spectrum [35]. Or, it can be attributed to the presence of excess precursors of Se ions at the boundary between CdTe and CdSe act as site trapping of charge carriers, which reduces the mobility of charge carriers and increases recombination rates, which decreases the intensity of the PL [46-49].

The particle sizes of CdTe QDs and CdTe/CdSe core-shell QDs was calculated using an empirical relationship [50]:

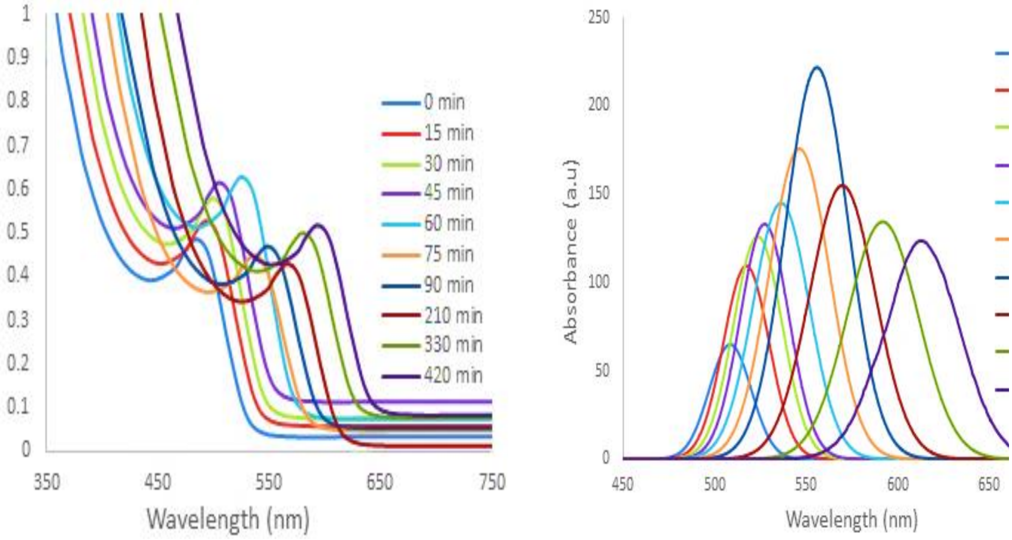
$$D\ (nm) = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.006)\lambda - (194.84) \qquad (\mathbf{1})$$

where D (nm) is the diameter of a QD sample and λ (nm) is the wavelength of the first excitonic absorption peak of the UV–vis absorption spectrum.



a **b**

Figure 1: (a) absorbance and (b) photoluminescence spectra of 3MPA-CdTeQDs at PH 12 with different reaction times (0, 15, 30, 45, 60, 75, 90, 210, 330, 430 min).



a **b**

Figure 2: (a) absorbance and (b) photoluminescence spectra of 3MPA-CdTe/CdSe QDs at PH 12 with different reaction times (0, 15, 30, 45, 60, 75, 90, 210, 330, 430 min).

Table 1: The optical properties of 3MPA-CdTe QDs and 3MPA-CdTe/CdSe QDs at pH 12.

3MPA-CdTe QDs

Reaction Time (min)	**Abs. Max. (nm)**	**PL. Max. (nm)**	**Peak Intensity (a.u)**	**FWHM (nm)**	**Stock Shift (nm)**	**E_g (eV) 1240/λ (nm)**	**Particle size (nm)**
0	488	522	126	35	34	2.37	1.97
15	498	525	192	39	27	2.36	2.28
30	502	528	293	43	26	2.34	2.39
45	509	531	383	40	22	2.33	2.57
60	516	533	416	38	17	2.32	2.72
75	522	538	465	40	16	2.30	2.84
90	533	542	509	43	9	2.28	3.02
210	547	558	602	44	11	2.22	3.20
330	553	565	645	45	12	2.19	3.27
420	564	576	638	47	12	2.15	3.37

3MPA-CdTe/CdSe QDs

Reaction Time (min)	**Abs. Max. (nm)**	**PL. Max. (nm)**	**Peak Intensity (a.u)**	**FWHM (nm)**	**Stock Shift (nm)**	**E_g (eV) 1240/λ (nm)**	Particle size (nm)
0	484	510	64	27	30	2.41	1.83
15	493	518	109	29	25	2.39	2.13
30	499	523	125	31	24	2.37	2.31
45	505	530	133	33	25	2.33	2.47
60	525	538	145	36	13	2.30	2.89
75	536	548	175	38	12	2.26	3.07
90	548	559	221	40	11	2.21	3.22
210	566	576	154	42	10	2.15	3.39
330	580	593	134	45	13	2.09	3.50
420	593	602	123	48	9	2.05	3.60

4. Conclusions

A regular spectrum increase was observed in the absorbance and the intensity of the peaks of 3MPA-CdTe QDs. In contrast, there is a difference in the absorbance and intensity of the peaks in 3MPA-CdTe/CdSe QDs. These differences may be attributed to excess precursors of Se ions at the boundary between CdTe and CdSe acting as site trapping for charge carriers, which reduces the mobility of charge carriers and increases recombination rates, decreasing the intensity of the PL. The optical examinations showed shifting toward higher wavelength values, increased QDs size, and a decreased energy gap with increased reaction time.

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Conflict of Interest

The authors declare that they have no conflict of interest.

References

1. H. N. Noori and A. F. Abdulameer, Chem. Methodol. **6**, 842 (2022).
2. M. a. H. Al-Beayaty, Iraqi J. Sci. **62**, 4323 (2021).

3. N. K. Abass, Z. J. Shanan, T. H. Mohammed, and L. K. Abbas, Baghdad Sci. J. **15**, 0198 (2018).
4. R. Al-Obaidy, A. J. Haider, S. Al-Musawi, and N. Arsad, Sci. Rep. **13**, 3180 (2023).
5. A. I. Ekimov, J. E. T. P. Lett. **34**, 345 (1981).
6. S. Baskoutas and A. F. Terzis, J. Appl. Phys. **99**, 013708 (2006).
7. S. Chaturvedi, P. N. Dave, and N. K. Shah, J. Saudi Chem. Soci. **16**, 307 (2012).
8. H. Asano, S. Tsukuda, M. Kita, S. Fujimoto, and T. Omata, A. C. S. omega **3**, 6703 (2018).
9. S. Xiaofang, Micro. Nano Lett. **7**, 137 (2012).
10. G. E. J. Poinern, *A Laboratory Course in Nanoscience and Nanotechnology* (Perth, Western Australia, CRC Press, 2014).
11. Y. Zheng, S. Gao, and J. Y. Ying, Advan. Mat. **19**, 376 (2007).
12. M. Gao, C. Lesser, S. Kirstein, H. Möhwald, A. L. Rogach, and H. Weller, J. Appl. Phys. **87**, 2297 (2000).
13. W. Chen, A. G. Joly, and S. Wang, Encyclop. Nanosci. Nanotech. **4**, 689 (2004).
14. S. Kini, S. D. Kulkarni, V. Ganiga, T. Nagarakshit, and S. Chidangil, Mat. Res. Bullet. **110**, 57 (2019).
15. P. Sarkar, M. Springborg, and G. Seifert, Chem. Phys. Lett. **405**, 103 (2005).
16. J. Li and L.-W. Wang, Appl. Phys. Lett. **84**, 3648 (2004).
17. N. Mcelroy, R. Page, D. Espinbarro-Valazquez, E. Lewis, S. Haigh, P. O'brien, and D. Binks, Thin Sol. Fil. **560**, 65 (2014).
18. A. Ayyaswamy, S. Ganapathy, A. Alsalme, A. Alghamdi, and J. Ramasamy, Superlatt. Microstruc. **88**, 634 (2015).
19. N. Kumar and S. Kumbhat, *Essentials in Nanoscience and Nanotechnology* (Hoboken, New Jersey, USA, John Wiley & Sons, 2016).
20. J. M. Baruah and J. Narayan, Mat. Res. Expr. **6**, 095082 (2019).
21. N. Husham, N. Noori, and F. A. Ammer, Iraqi J. Sci. **64**, 1 (2023).
22. Z. M. Khan, S. A. Khan, and M. Zulfequar, Mat. Sci. Semicon. Proce. **57**, 190 (2017).
23. A. M. Smith, H. Duan, A. M. Mohs, and S. Nie, Advan. Drug Deliv. Rev. **60**, 1226 (2008).
24. M. Green, J. Mat. Chem. **20**, 5797 (2010).
25. J. W. Kyobe, E. B. Mubofu, Y. M. Makame, S. Mlowe, and N. Revaprasadu, New J. Chem. **39**, 7251 (2015).
26. C. Ge, M. Xu, J. Liu, J. Lei, and H. Ju, Chem. Communic. **2008**, 450 (2008).
27. B. Gao, C. Shen, Y. Yang, S. Yuan, and G. Chen, in International Congress on Energy Efficiency and Energy Related Materials (ENEFM2013) Proceedings (Antalya, Turkey Springer, 2014). p. 9.
28. S. Mustapha, M. Ndamitso, A. Abdulkareem, J. Tijani, D. Shuaib, A. Mohammed, and A. Sumaila, Advan. Nat. Sci. Nanosci. Nanotech. **10**, 045013 (2019).
29. V. Ncapayi, S. O. Oluwafemi, S. P. Songca, and T. Kodama, MRS Online Proce. Lib. **1748**, 69 (2015).
30. P. Roy, M. Virmani, and P. P. Pillai, Chem. Sci. **14**, 5167 (2023).
31. C. De Mello Donega, S. G. Hickey, S. F. Wuister, D. Vanmaekelbergh, and A. Meijerink, J. Phys.l Chem. B **107**, 489 (2003).
32. A. M. Kadim and W. R. Saleh, Iraqi J. Sci. **58**, 1207 (2017).
33. S. Kiprotich, M. O. Onani, and F. B. Dejene, Phys. B: Conden. Matt. **535**, 202 (2018).
34. Y. Lv, Y. Cheng, K. Lv, G. Zhang, and J. Wu, Micromachines **13**, 788 (2022).
35. D. Das and R. K. Dutta, J. Photochem. Photobio. A: Chem. **400**, 112709 (2020).

36. N. Mntungwa, P. V. Rajasekhar, and N. Revaprasadu, Mat. Chem. Phys. **126**, 500 (2011).
37. O. S. Oluwafemi, O. A. Daramola, and V. Ncapayi, Mat. Lett. **133**, 9 (2014).
38. W. Mao, J. Guo, W. Yang, C. Wang, J. He, and J. Chen, Nanotechnology **18**, 485611 (2007).
39. S. Subramanian, S. Ganapathy, M. Rajaram, and A. Ayyaswamy, Mat. Chem. Phys. **249**, 123127 (2020).
40. B. J. Kumar and H. Mahesh, Superlatt. Microstruc. **104**, 118 (2017).
41. F. A. Hassan, A. N. Naje, and R. K. Ibrahim, Iraqi J. Sci. **57**, 1198 (2016).
42. N. Ca, N. Hien, N. Luyen, V. Lien, L. Thanh, P. Do, N. Bau, and T. Pham, J. Allo. Comp. **787**, 823 (2019).
43. S. J. Lim, M. U. Zahid, P. Le, L. Ma, D. Entenberg, A. S. Harney, J. Condeelis, and A. M. Smith, Nat. commun. **6**, 8210 (2015).
44. V. Ncapayi, S. Parani, S. P. Songca, T. Kodama, and O. S. Oluwafemi, Mat. Lett. **189**, 168 (2017).
45. A. Al-Douri, Iraqi J. Phys. **9**, 18 (2011).
46. A. M. Smith, A. M. Mohs, and S. Nie, Nat. Nanotech. **4**, 56 (2009).
47. P. Devaraji, R. Gao, L. Xiong, X. Jia, L. Huang, W. Chen, S. Liu, and L. Mao, Int. J. Hyd. Ener. **46**, 14369 (2021).
48. H. N. Noori and A. F. Abdulameer, Iraqi J. Sci. **64**, 653 (2023).
49. D. Bahnemann and A. O. T. Patrocinio, *Springer Handbook of Inorganic Photochemistry* (Switzerland, Springer Nature, 2022).
50. W. W. Yu, L. Qu, W. Guo, and X. Peng, Chem. Mat. **15**, 2854 (2003).

دراسة الخصائص البصرية للنقاط الكمومية *3MPA CdTe* و*3MPA CdTe/CdSe* عند *PH 12* في فترات زمنية مختلفة

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الخلاصة

يهدف هذا البحث إلى دراسة الخصائص البصرية للنقاط الكمومية لأشباه الموصلات (QDs) المكونة من هياكل غلاف قلب CdTe و CdTe / CdSe . في هذه الدراسة تم استخدام طريقة الارتداد لتوليف هذه الجسيمات النانوية بهدف فهم عملية النمو من خلال مراقبة خصائصها البصرية على مدى فترات متفاوتة عند درجة الحموضة 12. على وجه التحديد، يتم تقييم التطور البصري لهذه QDs باستخدام اللمعان الضوئي (PL) والأشعة فوق البنفسجية و(UV) التحليل الطيفي. بالنسبة لـCdTe QDs ، لوحظ وجود امتصاص ثابت وزيادة شدة الذروة عبر الطيف بمرور الوقت. على العكس من ذلك، أظهرت QDs CdTe / CdSe اختلافات شدة الامتصاص المميزة والذروة. قد تنجم هذه التباينات عن عدم انتظام تكوين طبقات السيلينيوم (Se) حول CdTe QDs خلال مراحل النمو، مما يحتمل أن يحفز التبريد في طيف الانبعاث. كشفت الفحوصات البصرية النقاب عن انزياح أحمرواضح تجاه قيم الطول الموجي الأعلى مع تقدم التفاعل. اقترن هذا التحول الطيفي بتوسيع في حجم QDs وانخفاض فجوة الطاقة. أتاح استخدام تقنيات تحليل PL وUV إجراء دراسة شاملة للسمات البصرية لأنظمة CdTe و CdTe / CdSe QD . تؤكد النتائج التي توصلنا إليها على تأثير ظروف النمو ومواد الغلاف على الخواص البصرية لـ QDs. توفر التغييرات الملحوظة في الامتصاصية، وشدة الذروة، وقيم الطول الموجي، وحجم QDs، وفجوة الطاقة مع زيادة وقت رد الفعل، رؤى قيمة حول ديناميكيات النمو لهياكل QDs .

الكلمات المفتاحية: طريقة الارتجاع، النقاط الكمومية، الطريقة المائية، الرقم الهيدروجيني، الأشعة فوق البنفسجية.