

Broadening Spectral Line Method for Determination Structural Parameters and Electronic Transitions in CdSe Artificial Atom

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Abstract: Multi layers CdSe artificial atoms system prepared using Spin coating method. Using W-H method, which based on XRD Broadening line profile, structural parameters of FTO/CdSe system were calculated. XRD spectrum reveal that CdSe nanoparticles have hexagonal structure, have high strain, show deposition layer on other do more stress and strain (Crystallization size (6.16 \AA), lattice constant $C(7.16 \text{ \AA})$, effective strain ($0.07377 (\text{lin}^{-2} \text{ m}^{-4})$) between the nano crystals and dislocation (irregular) ($26.443 \times 10^{20} (\text{lin} \cdot \text{m}^{-2})$) were determined), which confirm more later by another spectroscopic method. By doing fitting between experimental and theoretical absorption using Gaussian profile and Doppler broadening line. Different electronic transitions were deduced and other broadening curve were studying such as effect of particle size of artificial atoms, with doing more accurate fitting reveals existence of two intensities lines attributed to diffusion layer between FTO and CdSe artificial atoms.

Keywords: CdSe, Artificial Atoms, XRD Broadening, Absorption Spectra, Doppler Broadening

1. Introduction

Colloidal semiconductor nanocrystals (also known as quantum dots, QDs) are generally composed of II–VI and III–V elements, which exhibit strongly size dependent optical and electrical properties [1]. Chemically synthesis of high quality semiconductor nanocrystals (NCs) has shown potential applications in thin film light-emitting devices [2, 3], non-linear optical devices [4] and solar cells. Recently, considerable attention has been exerted on using QDs as fluorescent labels for biological applications [5]. A large number of high quality QDs such as CdSe, CdTe were successfully synthesized by organometallic approach [6]. The as-prepared QDs possess high quantum yield (QY) up to 50% (even up to 85%) [7] and sharp emission spectra. The height and energy between different energy levels varies inversely with the size of Q-dot [8]. The quantum dots of the same material, but with different sizes, can emit light of different colours. The physical reason is the quantum confinement effect. The larger dots have lower energy in the fluorescence

spectrum. The smaller dots emit bluer higher energy light [9]. The lifetime of fluorescence is determined by the size of the quantum dot. Larger dots have more closely spaced energy levels in which the electron-hole pair can be trapped. Hence, electron-hole pairs in larger dots live longer causing larger dots to show a longer lifetime. Similar to a molecule, a quantum dot has both a quantized energy spectrum and a quantized density of electronic states near the edge of the band gap. Quantum dots can be synthesized with larger shells. The shell thickness has shown direct correlation to the lifetime and emission intensity. A main advantage with quantum dots is that, because of the high level of control possible over the size of the crystals produced, it is possible to have very precise control over the conductive properties of the material.

Optical absorption in room temperature artificial atoms (quantum dots) is importance key for applications of these materials including photovoltaic. Light emitting diodes, and fluorescent tagging [10]. A particularly useful feature of these

materials is that the optical transitions broadened over a range comparable to the spacing between them, such that they strongly absorb light over a wide energy range. This feature, however, makes it difficult to study the origins of the broadening because individual transitions are difficult to discern. Previous work has characterized the transitions for ensembles of NCQDs of various radii. Here, we investigate both spectra of XRD and absorption spectrum of transitions in individual Nano crystals, using a photoluminescence excitation (PL) technique. The experiment reveals the broadening the transition in the absence of ensemble averaging and the variation in transition energies that gives rise to the ensemble broadening.

To increase intensity of emission light and efficiency of PL spectra of transport hole or electrons layer insert between electrode and (P or N) semiconductor layer. In this paper, Homogeneous and inhomogeneous of optical absorption profile broadening at room temperature of FTO/TiO₂(Polystyrene)/CdSe(QDs)/PANI/EL LEDs investigated to show influence of quantum confinement on absorption spectra. Using W-H method to illustrate the effect of confinement on different layer structure.

2. Materials

Microscopic slices, K₂Cr₂O₇ for cleaning glass slides, HF (fluoric acid), SnCl₂·2H₂O, Ethylenglycol, polyaniline (PANI), polyvinyl alcohol (PVA), CuCl₂, KI, Se powder, Cd(CH₃COO)₂·4H₂O, Hydrazen, deionized water.

3. Synthesis of FTO/TiO₂(Polystyrene)/CdSe (Artificial Atoms)/EL/Ag

- Preparing Transparent Conducting Fluoride Tin Oxide (FTO):

Microscopic slices was cleaned using K₂Cr₂O₇, then it's emerge diluted fluoric acid (HF) for 10 minutes for scratch external surface of Microscopic slices. After that Microscopic slice were heated put on electrical oven to 500C°. SnCl₂·2H₂O (5gr) solved in 20ml of Ethylenglycol and sprayed on Microscopic slices several times each 5 minutes. The deposited resistance film SnO₂ measured and its (13–40)Ω.

- Preparation TiO₂(Polystyrene):

TiO₂ (Polystyrene) Colloidal solution was prepared by solve 0.1 mol of TiO₂ in 50ml of ethanol with heated to 50C°.

- Preparation CdSe artificial atoms:

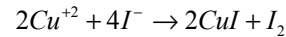
Artificial atoms of CdSe were prepared by chemical solutions method. Cadmium Citrate (Cd (CH₃COO)₂·4H₂O) used as the cadmium source and sodium selenosulfate (Na₂SeSO₃) was chosen as the selenium source. Cadmium Citrate (22.8 gr) was solved in 100 ml of deionized water called solution (A). Sodium selenosulfate which was prepared by solving Na₂SO₃(12.6 gr) in 100 ml of deionized

water, adding selenium powder (7.96 gr) to previous solution refluxed at 70C° for 3 hours, red wine solution will appear called solution (B). Solution (A) (20ml) was added to solution (B) (5ml), ethylene glycol (5 ml) hydrazine hydrate (5ml) were added to previous. CdSe colloidal Solution was adjusted 10 by adding 1 ml NaOH solution.

- Preparation of Electrolyte Layer (EL):

PVA powder (5gr) solved in 100 ml of deionized water, stirred with magnetic stirrer at 70C° for 2 h. previous solution was aged for 1h at room temperature called solution (A). CuCl₂·2H₂O (5gr) was solved in 100ml of deionized water at room temperature called solution (B). 5 gr of KI was solved in 100ml of deionized water at room temperature called solution (C).

10ml of solution (B) added to 30ml solution (A) with keep maxing for 1h at room temperature. Then solution (c) added to previous solution 2 h later drop wise into the Reaction vessel satisfying The ratio C=KI/CuCl₂ (C = 10), followed by stirring for another 2 h. The production process of CuI was according to the following reaction:



- -Preparing FTO/TiO₂(Polystyrene)/CdSe (artificial atoms) /EL/Ag:

Using spin coating method for prepared FTO/TiO₂(Polystyrene)/CdSe (artificial atoms) /EL/Ag. as it show in Figure 1.

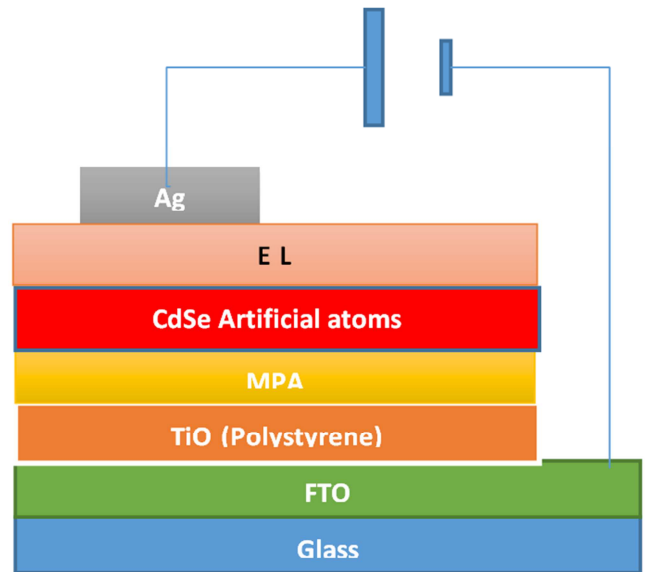


Figure 1. Shows FTO/TiO₂/MPA/CdSe /EL LEDs.

4. XRD Spectrum of FTO/CdSe System

The X-ray diffraction (XRD) spectrum of FTO/CdSe film was recorded by Philips system using Cu Kα (λ=1.54056Å) radiation with 2θ in the range 20-80°. Figure 2 show (XRD) spectrum, which reveal CdSe sample is polycrystalline in nature having all peaks corresponding to the specific planes, The extra peaks observed for CdSe artificial atoms at 2θ

(degree) $2\theta^\circ = 29.18^\circ, 41.75^\circ, 48.75^\circ$ with maximum intensity peak which corresponding oriented planes (101), (102), (112) planes respectively, and for 2θ equal

$2\theta^\circ = 25^\circ, 35^\circ, 37^\circ, 52^\circ, 62.1^\circ, 65.8^\circ$ are different angles for FTO corresponding (110), (101), (200), (221), (310), (301) Respectively.

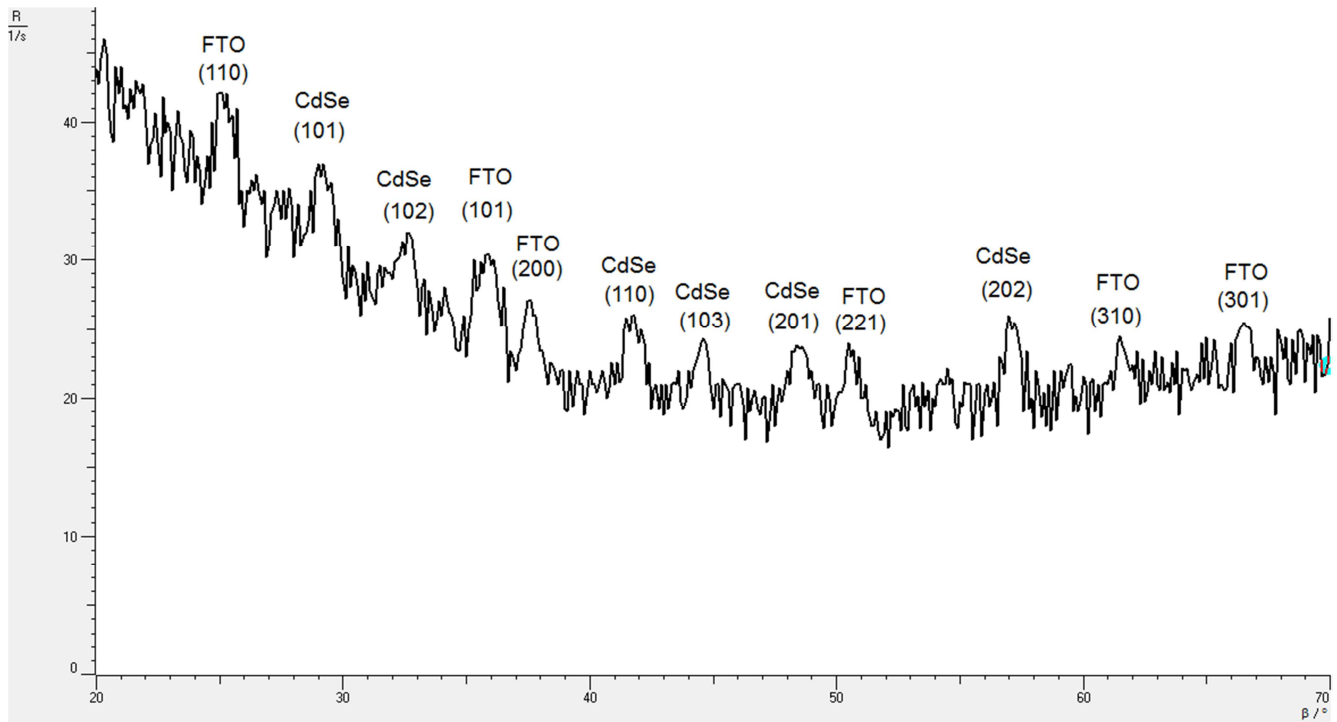


Figure 2. XRD spectrum of FTO/CdSe.

The lattice spacing, d , calculated from the Bragg's formula [11]:

For first peak $d=3.06\text{\AA}$, $n=1$, $2\theta=29.18^\circ$ for CdSe artificial atoms. For FTO $d=3.56\text{\AA}$ at $n=1$, $2\theta=25^\circ$

$$d = \frac{n\lambda}{2 \sin \theta}$$

The peak broadening in XRD patterns may arise from several reasons such as smaller crystallite size, instrumental

error and strain broadening: $\beta_{tot} = \beta_v + \beta_s + \beta_m$. As in the present case, proper precautions have been taken into account during scanning such as slow scan rate. Therefore, the observed broadening (figure 2) is due to the strain and smaller crystallite size, where their contribution to peak broadening is independent of each other. Therefore, total broadening can be written as sum of these two as $\beta_{total} = \beta_{strain} + \beta_{crystallite\ size}$. By neglected broadening instrument, using Williamson-Hall (W-H) equation [12]:

$$\frac{\beta_{total} \cdot \cos \theta}{\lambda} = \frac{1}{D} + \frac{4\epsilon \cdot \sin \theta}{\lambda} \Rightarrow \beta_{total} \cdot \cos \theta = \frac{\lambda}{D} + 4\epsilon \cdot \sin \theta$$

Where ϵ is the effective strain present in the material, d the effective crystallite size, λ the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) and θ the diffraction angle. By plotting $\beta_{total} \cdot \cos \theta$ in function of $\sin \theta$, Negative slope of pure CdSe artificial atoms as shown in Figure 3 indicate the presence of effective compressive strain in the crystal lattice. Effective strain for CdSe artificial atoms $\epsilon_1 = 0.07377 \text{ (}\ln^{-2} \text{ m}^{-4}\text{)}$,

For FTO $\epsilon_2 = 0.00615 \text{ (}\ln^{-2} \text{ m}^{-4}\text{)}$. In materials science, a dislocation is a crystallographic defect, or irregularity, within a crystal structure. The presence of dislocations strongly influences many of the properties of materials. The dislocation density " δ " has been calculated by using the formula [13]: $\delta = \frac{15\epsilon}{D.a}$

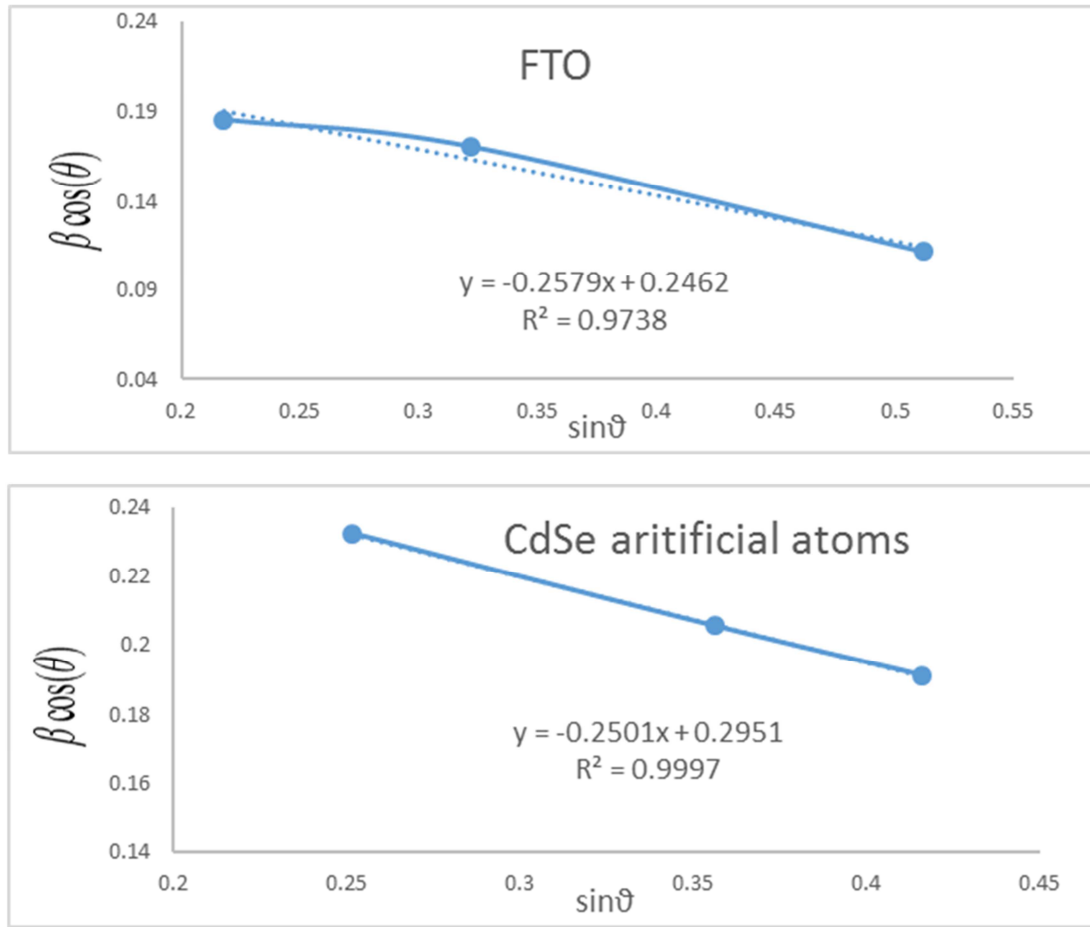


Figure 3. W-H plot for CdSe artificial atoms, FTO.

Where ε effective strain values, D The crystallite size, a hexagonal lattice constant for CdSe artificial atoms equal 4.29 \AA . The lattice constant C is determined for Wurtzite structure by the following expression [11]:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + \ell^2)}{c^2}$$

Where h, k and ℓ represent lattice planes (202) which corresponding with diffraction angle $2\theta = 56.8^\circ$. Lattice constant C is close to standard value 7.01 \AA . Table (1) show the different parameters calculated using W-H for both CdSe artificial atoms and FTO layer. It reveal the high strain

parameter of FTO and CdSe due to quantum confinement of one CdSe layer quantum confinement of CdSe artificial atoms. For FTO The lattice constant C is determined for hexagonal structure by the following expression [14]:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{\ell^2}{c^2}$$

Where h, k and ℓ represent lattice planes (101) which corresponding with diffraction angle $2\theta = 37.52^\circ$, $a = 4.73 \text{ \AA}$ for hexagonal lattice.

Table 1. Summary of XRD Spectrum.

	$\delta (\text{lin} \cdot \text{m}^{-2})$ dislocation density	$\varepsilon (\text{lin}^{-2} \text{ m}^{-4})$ effective strain	d (Å) lattice spacing	D (Å) Average crystallite size	C (Å) Lattice constant
CdSe (artificial atoms)	26.443×10^{20}	0.07377	3.06	6.16	7.16
FTO	29.65×10^{18}	0.00615	3.56	6.26	5.47

5. Absorption Spectra of FTO/TiO₂ (Polystyrene)/MPA/CdSe Artificial Atoms/EL LED

To know different process of broadening line in the matrix FTO/CdSe and to reveal these different broadening types Absorption spectra of FTO/TiO₂ (Polystyrene)/MPA/CdSe Artificial atoms/EL LED carried out using spectrophotometer (UV Win5 V5.2.0). Absorption spectrum Figure 4 reveals two peaks centered at wavelength (375-596) nm.

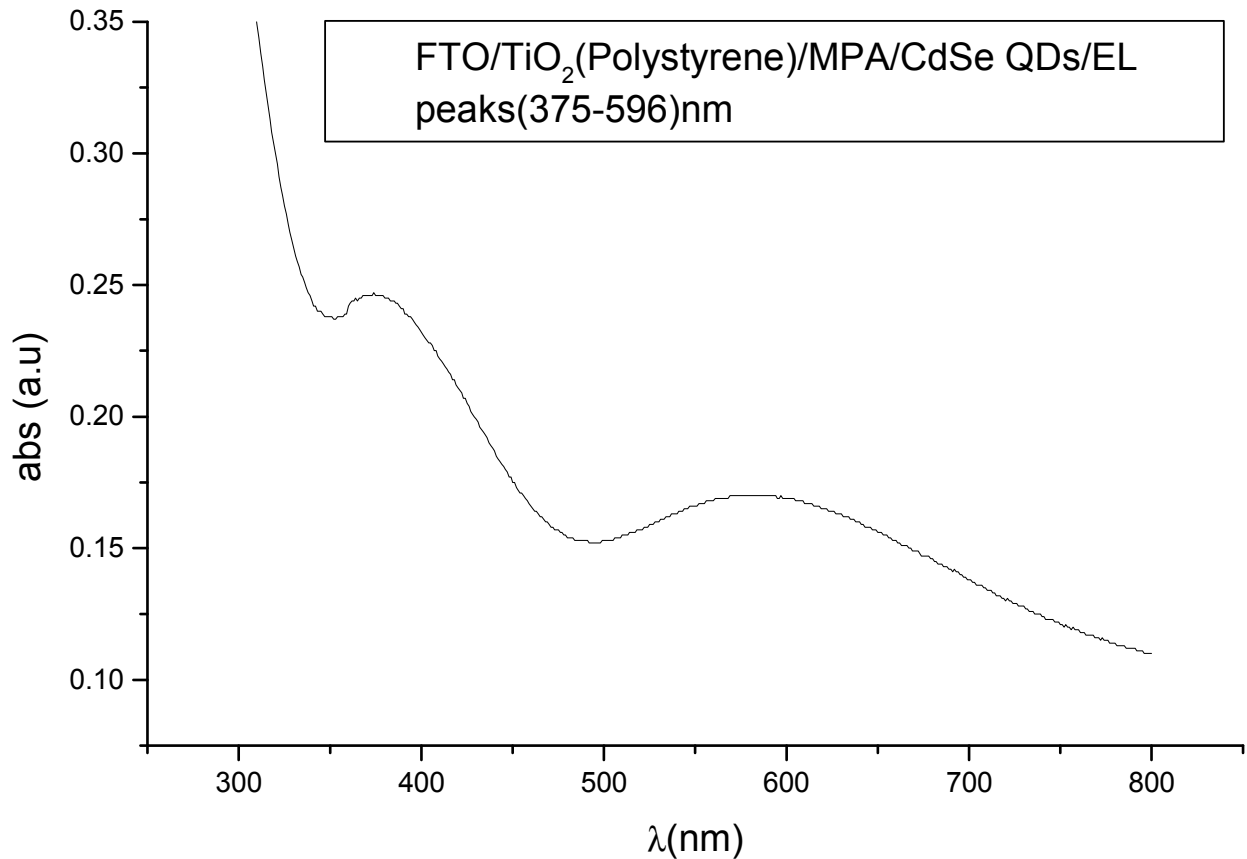


Figure 4. Absorption spectra of FTO/TiO₂(Polystyrene)/MPA/CdSe QDs/EL.

The broad absorption spectrum at 596 nm related to electronic transitions in CdSe artificial atoms the highest occupied molecular orbital (HOMO) originates from Se 4p atomic orbital's, and the lowest unoccupied molecular orbital (LUMO) from Cd 5s atomic orbitals. Those electronic states are strongly dependent on the size (the degree of confinement). Because increasing the aspect ratio only reduces confinement along the c-direction, some energy levels are sensitive to the length of the NR much more than others, and level crossing occurs. For HOMO levels, the levels consisting of a Se 4p component are more dependent on the length, by increasing the Nano rods length; the energy levels converge into several energy levels. This is a transition from zero-dimension confinement (0D) to one dimensional (1D), where a continuous band forms along the c-axis. For this reason, more versatile Nano electronic and optical devices, which combine the advantage of 0D and 1D confinement, can potentially be made using quantum NRs as building blocks [15]. Where the absorption peak at 375 nm due to direct transition for TiO₂. From figure (4) the high absorption peak at wavelength 300 nm related to FTO band-to-band transition. Result of homogeneous broadening in absorption spectra was caused for several reasons; quantum confinement and multi high barriers in stature of FTO/TiO₂/CdSe/EL system and different sizes of artificial atoms of CdSe.

6. Homogenous Broadening in Electronic Transitions in CdSe Artificial Atoms LEDs

To insure electronic transitions in CdSe artificial atoms which is found in structure of FTO/TiO₂/CdSe/EL system, theoretical energy of electronic transitions as in figure (5). By using Gaussian, profile for all theoretical energies transitions of CdSe artificial atoms [16], energy band gap of FTO and energy transition of TiO₂ with using experimental values from absorption spectra. When Doppler broadening is dominate, velocity distribution is dominate on line spectra. in these case experimental line spectral give by distribution of velocity for atoms or molecular as shown [9]:

$$I(\lambda) = I_0 \exp \left[-\frac{MC^2}{2KT} \left(\frac{\lambda - \lambda_0}{\lambda_0} \right)^2 \right]$$

Where $I(\lambda)$ is line spectra module (maximum intensities of line spectral). by use $\Delta\lambda = \lambda - \lambda_0$; FWHM

$$\Delta\lambda_D = 2\lambda_0 \left[\frac{2KT}{MC^2} \right]^{\frac{1}{2}}$$

$$\frac{\Delta\lambda_D}{\lambda_0} = \frac{\Delta v_0}{v_0} = 7.16 \times 10^{-7} \left[\frac{T}{M} \right]^{\frac{1}{2}} \Rightarrow \Delta\lambda_D = \lambda_0 \times 7.16 \times 10^{-7} \left[\frac{T}{M} \right]^{\frac{1}{2}}$$

Where T absolute temperature (300K). Table 1 show values of broadening in absorption wavelength peak.

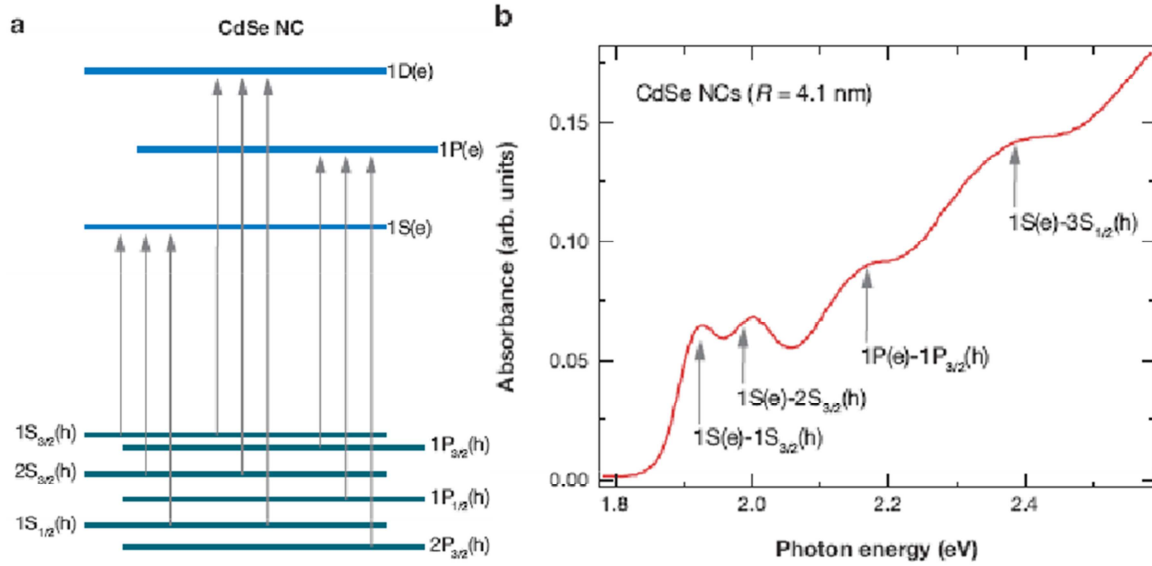


Figure 5. Electronic transition in CdSe artificial atoms and these energies.

Table 2. Shows absorption wavelength, their energy, electronic transitions and value of broadening in absorption wavelength peak.

λ_0 (nm)	E (eV)	Transition	$\Delta\lambda_D$ (nm)
280	4.4	FTO	0.0080
373	3.33	TiO ₂	0.0106
521	2.38	CdSe $1S(e) \rightarrow 3S_{1/2}(h)$	0.0146
568	2.18	$1P(e) \rightarrow 1P_{3/2}(h)$ CdSe	0.0161
620	2	$1S(e) \rightarrow 2S_{3/2}(h)$ CdSe	0.017
642	1.93	$1S(e) \rightarrow 1S_{3/2}(h)$ CdSe	0.018

Figure 6 show theoretical transitions (in different colors), experimental absorption spectra. From figure 6 reveal identified between experimental and theoretical transitions for all layers of LED structure. By taking Gaussian broadening for theoretical transitions for all layers of LED and compare with experimental absorption spectra by using Mathcad program. To do fitting between experimental and theoretical absorption spectra: first, different spectral line were traced using theoretical energy transitions for FTO and CdSe artificial atoms as it indicated in Table 1 and Figure (6) and using Gaussian shape which use Doppler broadening.

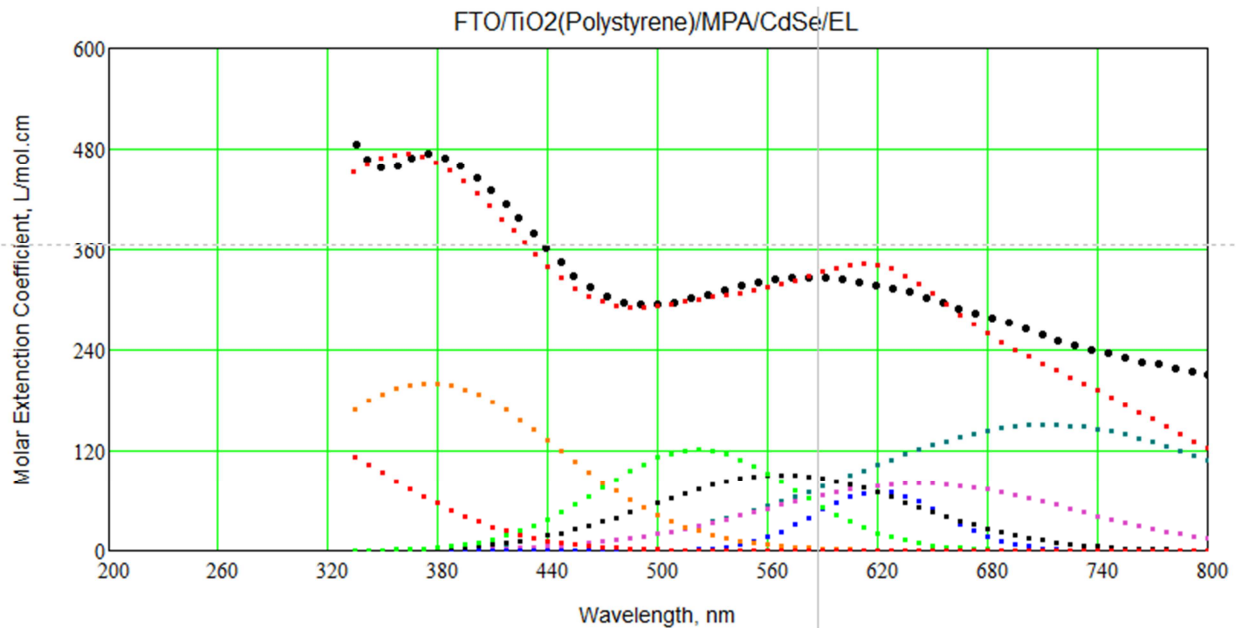


Figure 6. Theoretical transitions (in different colors) and experimental absorption spectra (black line).

Second, convolution were made for these traced lines and doing a rough fit with theoretical one. Figure 6 show the fitting between experimental and calculation absorption spectra as it clear the fitting was very well but not 100%.

Figure 7, show the 100% fitting between experimental and theoretical absorption spectra, it reveal two absorption peak located at 365 nm these small peak refer to absorption from diffused layer between FTO and CdSe layer.

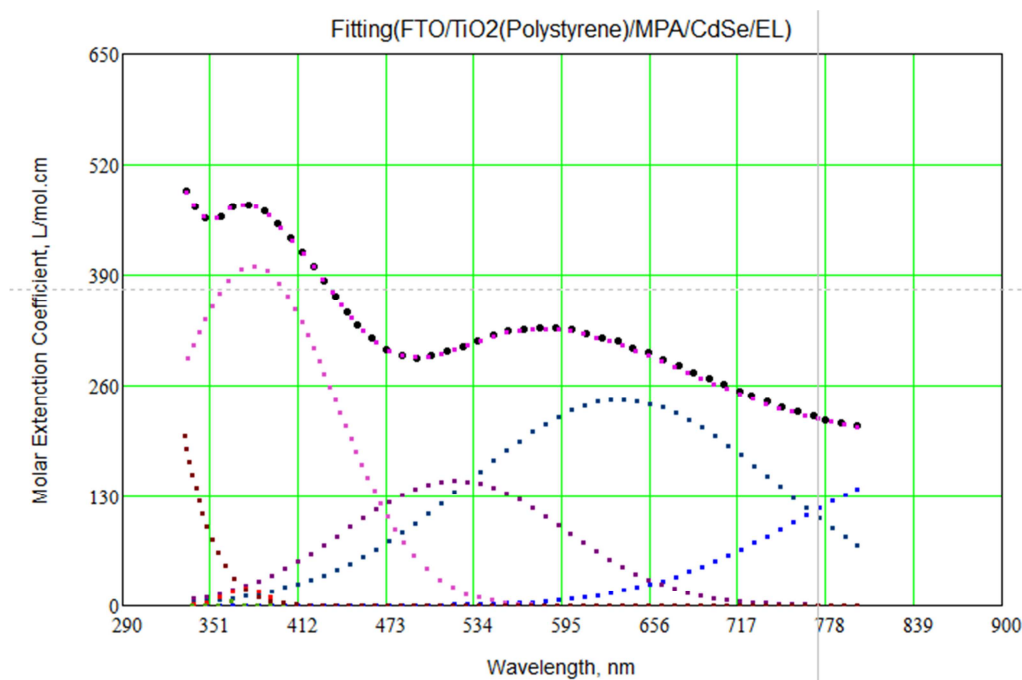


Figure 7. Fitting experimental absorption spectra with theoretical electronic transitions.

Also, note shift in energy transition that resulting of distribution different size of cluster atoms broadening, confinement broadening and Doppler broadening.

Table 3. Reveal theoretical electronic transitions, broadening energy transitions and difference between it in (eV).

Theoretical energy transitions (eV)	Broadening energy transitions (eV)	Energy shift (eV)
1.74 CdSe $4p(h) \rightarrow 5S_{\frac{1}{2}}(e)$	1.44 CdSe $4p(h) \rightarrow 5S_{\frac{1}{2}}(e)$	0.30
1.93 CdSe $1S(e) \rightarrow 1S_{\frac{3}{2}}(h)$	3.26 CdSe $1S(e) \rightarrow 1S_{\frac{3}{2}}(h)$	1.33
2 CdSe $1S(e) \rightarrow 2S_{\frac{3}{2}}(h)$	1.95 CdSe $1S(e) \rightarrow 2S_{\frac{3}{2}}(h)$	0.049
2.183 CdSe $1P(e) \rightarrow 1P_{\frac{3}{2}}(h)$	2.37 CdSe $1P(e) \rightarrow 1P_{\frac{3}{2}}(h)$	0.196
2.380 CdSe $1S(e) \rightarrow 3S_{\frac{1}{2}}(h)$	3.30 CdSe $1S(e) \rightarrow 3S_{\frac{1}{2}}(h)$	0.929
3.306 VB \rightarrow CB TiO_2	3.40 VB \rightarrow CB TiO_2	0.096
4.428 VB \rightarrow CB FTO	5.10 VB \rightarrow CB FTO	0.673

Ratio of Broadening, which due to size distribution and Doppler can neglected by comparing with quantum confinement broadening.

7. Conclusions

FTO/TiO₂(Polystyrene)/CdSe/EL system was prepared using spin coated method, quantum confinement effect on these structure was studied through XRD spectra using Williamson-Hall Method which: Produces crystallite size distribution. More accurately separates the instrumental and sample broadening effects. Gives a length average size rather than a volume average size. Broadening in absorption spectra lines reveal new electronic

transitions due to diffusion layer between CdSe artificial atoms and TiO₂ layers. There were energy shift between theoretical energy transitions and experimental absorption lines in CdSe artificial atom due to different effects such as; quantum confinement between layers of system, different size of cluster in one layer and diffusion between layers in particular between CdSe artificial atoms and TiO₂ layers.

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