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Morphological and Optical Properties of CdS Quantum Dots Synthesized with different pH values

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Abstract
Quantum dots (QDs) of cadmium sulfide (CdS) was prepared by chemical reaction method with different potential of hydrogen (pH) values. The morphological and optical measurements of cadmium sulfide QDs were considered by atomic force microscopy (AFM), ultraviolet-visible (UV-VIS.) and photoluminescence (PL) spectrometer respectively. The energy gap (Eg) was calculated from photoluminescence spectra were found to be about 2.7, 2.6 and 2.5 eV at pH values 8, 10 and 12 respectively for CdS QDs. The decreasing of energy gaps is rises from the effect the pH solution increases, which in turn leads to the shifted of the PL spectrum toward red shifted, which creates the energy bands at surface states are shallow bands. Fabrication of EL-device from CdS QDs with pH=8 was effective in efficient white light generation and intensity.

Keywords: Quantum dots, CdS, Luminescence, pH.

الخواص المورفولوجية والبصرية لكبريتيد الكادميوم نقاط كمية المحضرة بقيم مختلفة من الاس الهيدروجيني

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الخلاصة
تم تحضير نقاط كمية من كبريتيد الكادميوم بطريقة كيميائية بقيم مختلفة من الاس الهيدروجيني. شُخصت الخواص المورفولوجية والبصرية للنقاط كمية من كبريتيد الكادميوم بواسطة مجهر القوة الذري و مطياف الاشعة الفوق البنفسجية–المرئية و الانبعاثية على التوالي. تم حساب فجوات الطاقة من طيف الانبعاث وقيمها كانت 2,7 و 2,6 و 2,5 الكترون–فولط لقيم الاس الهيدروجيني 8 و 10 و 12 على التوالي للنقاط كمية من كبريتيد الكادميوم. هذا النقصان بقيم فجوات الطاقة ناشئ من زيادة تأثير الاس الهيدروجيني للمحلول، الذي يؤدي بدوره الى ازاحة طيف الانبعاث نحو المنطقة الحمراء من الطول الموجي مما يجعل حزم الطاقة في الحالات السطحية هي نطاقات ضحلة. تم تصميم نبيطة الانارة من النقاط كمية لكبريتيد الكادميوم مع الاس الهيدروجيني 8 والذي يؤثر بشكل فعال على كفاءة وشدة الضوء الابيض الناتج .

Introduction
Quantum Dots (QDs) are nanocrystals synthesized from semiconductor materials, such as cadmium sulfide (CdS), cadmium telluride (CdTe), cadmium selenide (CdSe), zinc sulfide (ZnS), etc., which is small (from 2 to 10 nm in diameter) enough to show quantum size confinement. Although

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nanocrystals' physical and chemical characteristics change, one of their big advantages over larger materials is that their size and surface can be quit controlled and properties tuned like quantum dots. Since of their excellent optical properties, QDs are of notice in many study fields such as, solar cells, organic light emitting devices (OLEDs), diode lasers, medical imaging, and quantum computing [1].
CdS QDs semiconductor have attracted significant interest because of their unique properties, which are not present in bulk materials from quantum confinement effect of charge carriers that differ clearly from those of bulk materials [1, 2].

The II–VI semiconductor having a broad optical band gap, rendering it a very achievement semiconductor material for optical and morphological application mainly in nanocrystalline form .CdS quantum dots has been mostly considered because of their high luminescence efficiency and easily adjustable luminescence from ultraviolet to near infrared region by nanocrystals sizes. The PL mechanism in CdS QDs is directed by an excitons fine structure interacting with multiple trap states [3].

The colloidal of QDs have highly luminescent efficiency is attractive materials because of their applications in optoelectronics, nonlinear optics, and biology. The electronic structure of colloidal QDs, which typically range from 3-12 nm in diameter, is dominated by quantum size effects [4].
The confinement size effect of quantum is reliable for the increase the energy difference between the energy band states and the band gap of QDs. A phenomenon strongly connected with the optical and electronic properties of the materials. The size effect of the quantum dots achieved by the chemical method can be organized by changing the ratio of pH effect to the surfactant agent [5].

Luminescent efficiency of QDs systems a significant and attractive class of luminescent semiconductors materials. They have confirmed excellent optical properties and higher photochemical strength than most organic emitters [6]. The color of light emitter depends on the size of the dots: the larger to minimize. As the dots minimize in size, the emitted light becomes shorter in wavelength, moving toward the blue region. Unique of the most interesting applications is the use of QDs as luminescent labels or fluorescent label sources for biological imaging applications [7].

However, the confined dimensions effect in a quantization of the bulk materials electronic bands and a broadening of the band gap between the valence band and conduction band, this is called a blue shift. This leads to changes the morphology and optical properties of QDs mechanism. However, most studies have attentive on the structure of QDs using different pH values. The pH effect is an essential effect on the physical presence of the QDs, as well as the chemical, optical and morphological properties of the quantum dots materials [8, 9].

In this work, the morphological and optical properties of CdS QDs, with different pH values of 8, 10 and 12, are scientifically considered with the effect of size dependent from absorption and photoluminescence spectra of QDs materials. The fabrication of white light emitting hybrid device is also represented for TPD: PMMA/CdS QDs obtained of acceptable intensity according to value of pH.

Experimental Work

Synthesis the CdS Quantum Dots

All materials used in this work were supplied from Fluka Company without further purification; the CdS QDs were prepared by mixing two chemical solutions of molarities 0.1 M. The first solution was prepared by dissolving 2.28 g of $CdCl_2$ in 100 ml distilled water, whereas the second solution was achieved by dissolving 0.76 g from thiourea powder $CS(NH_2)_2$ in 100 ml distilled water. The two solutions were mixed at 1:1 mole ratio in a three-neck flask and left on magnetic stirrer at temperature of about 90 ºC with continuous flowing of argon gas for about one hour. Where the solution at the beginning of the chemical reaction white color and after a 15 minutes turns the color of the solution to light yellow and after another 15 minutes turns the color change to yellow orange, this means that cadmium sulfide (CdS) nanostructures were formed and the chemical reaction as the following:-

$$\boldsymbol{CdCl_2 + H_2O + CS(NH_2)_2 \overset{\Delta}{\rightarrow} CdS + H_2S + Cl_2 + H_2O + NH_3 + CO_2}$$

The pH value for the prepared cadmium sulfide QDs was 5.5 this means that the solution is acidic, so the solution converted to base by adding alkaline solution of ammonium hydroxide (NH_4OH) drop by drop to the CdS QDs solution till having three values of pH 8, 10 and 12. The reason for the use of alkaline solutions instead of the acidic solution, because of the quantum dots decay rapidly in the acidic range.

To characterize the morphology of the CdS QDs films surface, CSPM AA3000 AFM supply by Angstrom Company was used. The optical measurements of CdS QDs were determined using OPTIMA SP- 3000 UV–VIS. spectrophotometer in the spectral range (200–1100) nm, while the PL spectrum was taken by SL 174 spectrofluorometer covering a range from (300–900) nm.

Morphological Measurements

Atomic Force Microscope (AFM)

The AFM images of the CdS QDs films with different pH values give a good indicator for formation of the CdS QDs. The average grain size determined from AFM is about 1.2, 3.42 and 6 nm of pH values 8, 10 and 12 respectively, as revealed in Figure- (1 a, b and c). The histograms of the percentage of CdS QDs as a function of the grain size, illustrate that the grains size influenced by increasing the pH values. Table-1 shows a summary of the AFM information measurements for CdS QDs samples.

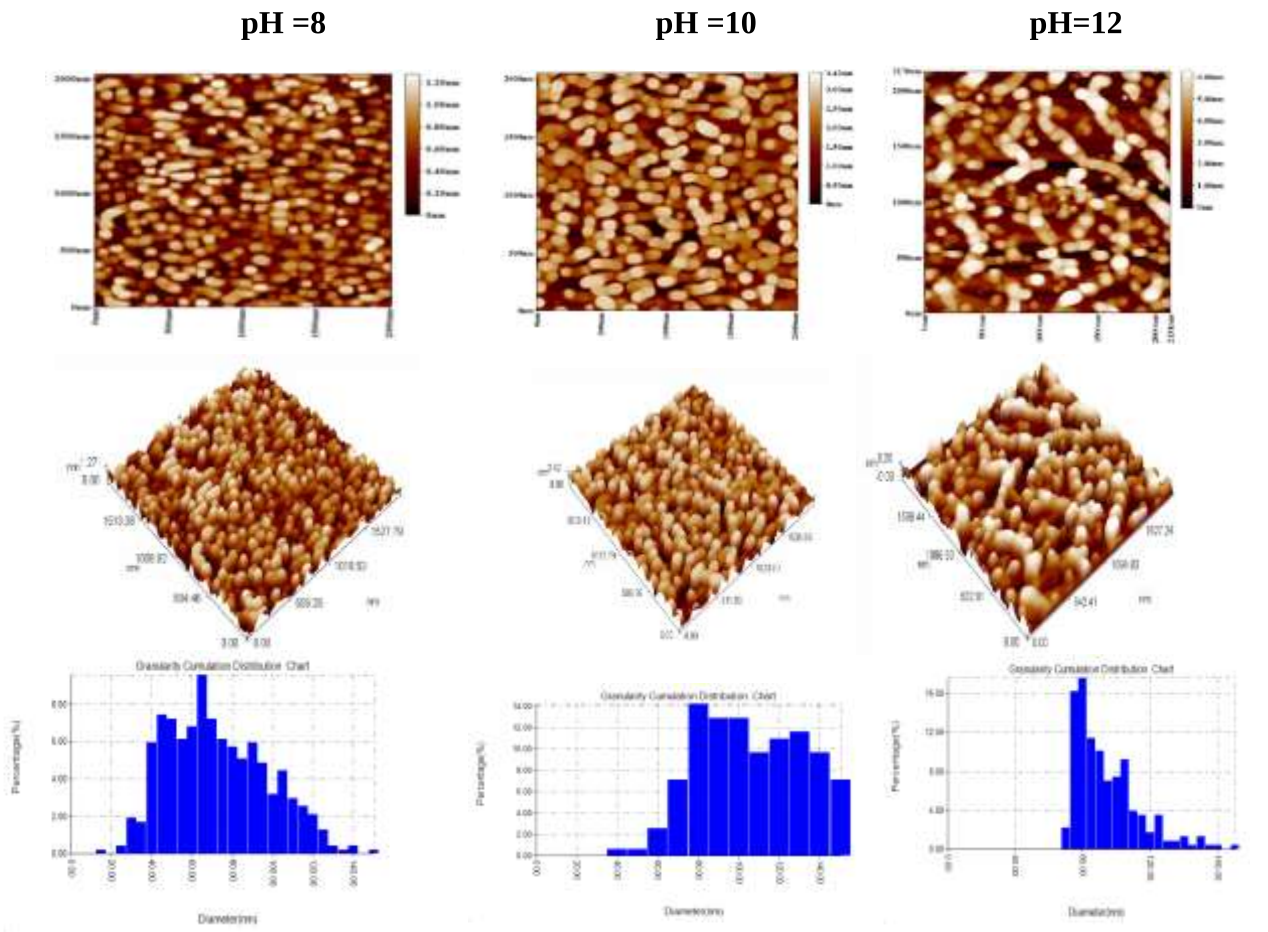

Figure 1- 2D, 3D and size distribution histogram AFM images of CdS QDs with different values of pH: 8, 10 and 12.

Table1- Summary of the AFM information of CdS QDs.

Sample	Roughness Average Sa (nm)	Root Mean Square Sq (nm)	Ten Point High Sz (nm)	Average Diameter D (nm)
8	0.25	0.29	1.25	55.12
10	0.64	0.77	2.22	61.02
12	1.5	1.73	3.42	74.9

Table-1 reveals that the average diameter of the grains increases when the pH value increase whereas the lowest diameter will be at pH value is 8. This is may be certified to the confinement size of CdS

QDs with decreases of pH values. It is also noticed that increasing the pH value increase the roughness of the film as well the average diameter of grains due to the effect of pH on the material.

Optical Measurements

The absorbance of the CdS samples was measured using OPTIMA SP-3000 UV-VIS. spectrophotometer supplied by Optima Company, covering a range from (300-1200) nm.

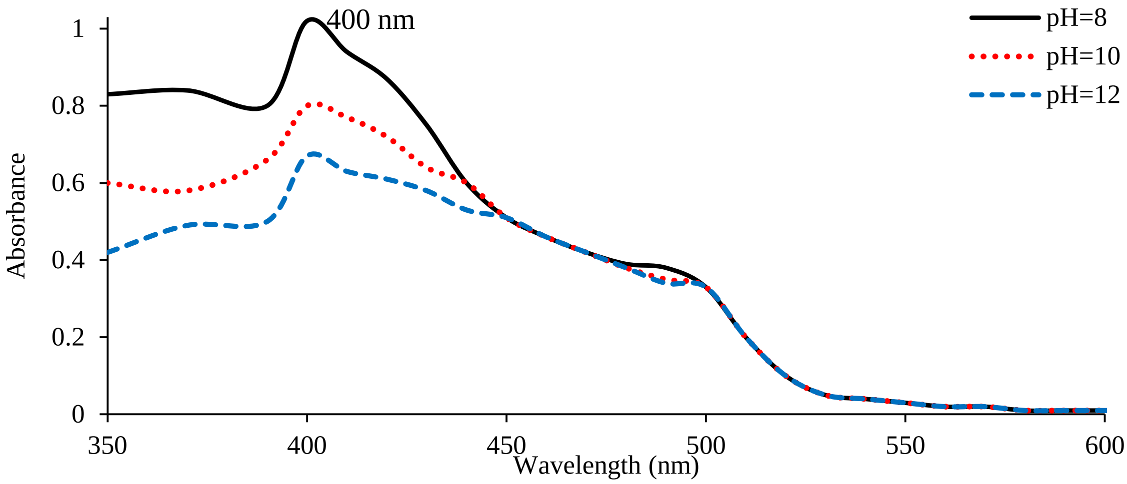

Figure 2- Absorption of CdS QDs with different values of pH (8, 10 and 12).

It is can be noticed from the Figure -1, the absorbance spectrum of CdS QDs illustration high absorbance in the visible range (400-490) nm and drastically decreasing till about 580 nm where there is no absorbance. The spectrum of CdS QDs shows exact absorption feature at 400 nm which is considerably blue-shifted by about 50 nm relative to the peak absorption of bulk CdS which is at 450 nm. The absorption peak of cadmium sulfide decreased with increasing the pH values. This means that the energy gap also decreases accordingly to the increase of solution pH value of the solution. These results were in a good agreement recommended by the other researcher [10, 11].

The photoluminescence spectrum of the cadmium sulfide QDs shows in Figure -3. In this figure at pH=8 the band transition is centered at 460 nm and other peaks represent the surface states and this result not far away form the values mentioned by [12]. In the other cases, at pH values of 10 and 12, the peaks of direct transition goes toward red shift at 470 and 480 nm respectively, while the other peaks represented the shallow bands at surface states in energy gap. The photoluminescence spectra with different pH include two different bands, the surface states emission of CdS nanocrystals and the emission of intrinsic [5].

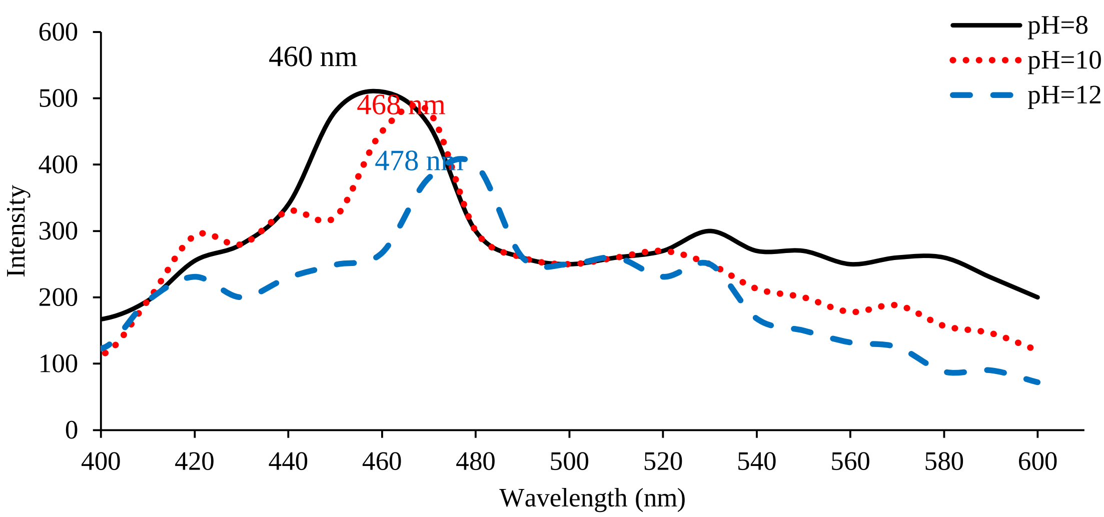

Figure 3- PL of CdS QDs with different values of pH (8, 10 and 12).

This means that when the pH solution increased, the concentration of the solution also increases according to the solution color as shown in Figures -4, which indicate a decrease in the intensity and energy gap of QDs. The energy gap was calculated from PL according to the relation (E=1240/λ (nm)) were found to be about 2.69, 2.65 and 2.59 eV for pH values of 8, 10 and 12 respectively of CdS QDs.

Figure 4- A photograph plate for samples of CdS QDs with different pH values (8, 10 and 12).

According to results above and depends of the confinement size effect of QDs were used to fabricated of TPD: PMMA/CdS hybrid junction device (CdS at pH=8 is better compared with other values in morphological and optical properties) to study the electroluminescence of light emitting device and the recombination process between the carries of charge in hybrid device as follow as:-
Figure -5 represented the configuration consists of two layers deposited successively on the ITO glass substrate by phase segregation method using spin coating. The first layer was of TPD mixed with PMMA, while the second layer was 0.05%wt QDs (each time using CdS QDs with pH=8).

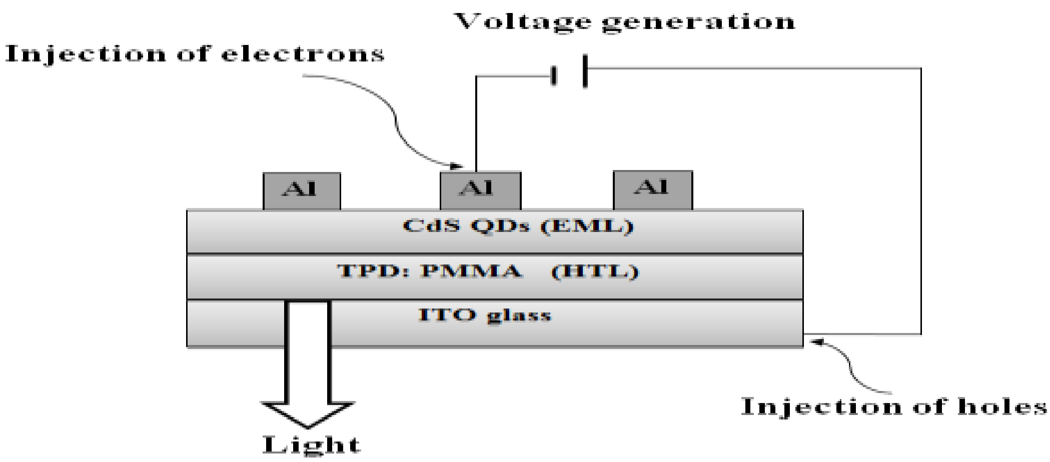

Figure 5- Structure of hybrid junction devices using CdS QDs.

The EL measurements shown in Figure -6 were carried out using a photomultiplier detector at room temperature under forward bias voltage of 8.4V. This voltage represents the upper limit for the light which has been obtained experimentally from the 1TPD:1PMMA:0.05%wt CdS with pH values 8 hybrid junction devices white light emission.

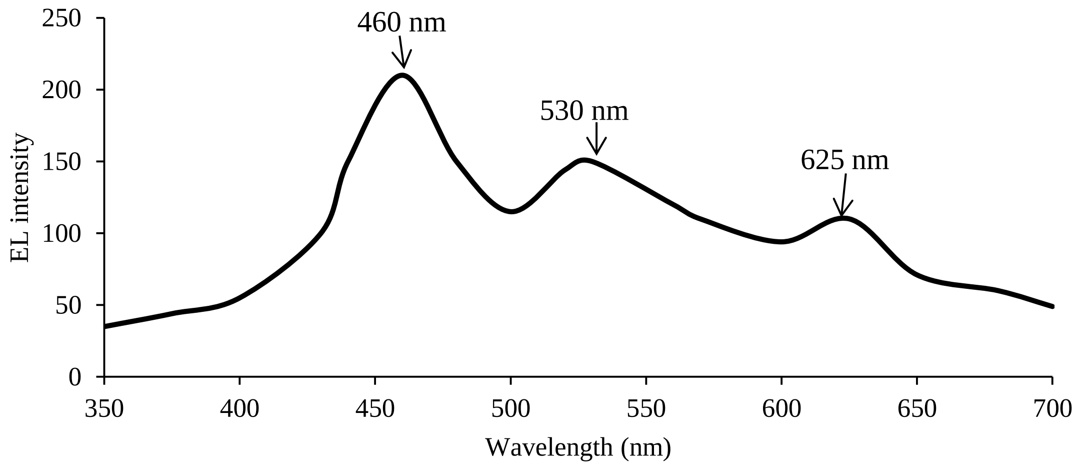

Figure 6- EL of TPD: PMMA/CdS hybrid device.

The emission in Figure-6 may be attributed to the increasing of the diffusion current which increases the production of excitons between the valance band of holes in higher occupied molecular orbital (HOMO) level, and conduction band of electrons in lower unoccupied molecular orbital (LUMO) level speedily moving towards of QDs. The energy released from the recombination of the charge transfer (CT) excitons is resonantly transferred to the proximal electrons in conduction band of the QDs through an Auger process to produce electrons with sufficiently high energy to inject into the lower unoccupied molecular orbital (LUMO) of TPD. These electrons then radioactively recombine with holes in the HOMO of the polymer, resulting in emission of photons with energy equal to the HOMO-LUMO gap of the TPD [13, 14].

Conclusion

In this work, the pH effect plays an essential role in changing the chemical, morphological and optical properties of CdS QDs. Increasing the pH value of CdS QDs leads to a change in the concentration of CdS QDs solution, which reduces the quantum efficiency of the QDs. The absorption spectra show that the size of prepared quantum dots depends on pH effect. The photoluminescence spectra with different pH include two different bands, the surface states emission of CdS nanocrystals and the emission of intrinsic. Fabrication of EL-device from semiconductors material (CdS QDs) and hole injection organic polymer (TPD) was effective in the intensity of white light generation.

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