Characterization of CdS quantum dots prepared by a Chemical Method

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Abstract

The CdS quantum dots were prepared by chemical reaction of cadmium oleylamine (Cd –oleylamine complex) with the sulfite-oleylamine (S-oleylamine) with 1:6 mole ratios. The optical properties structure and spectroscopy of the product quantum dot were studied. The results show the dependence of the optical properties on the crystal dimension and the formation of the trap states in the energy band gap.

Keywords
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خواص نقاط كبريتيد الكادميوم الكمية المحضرة بوساطة الطريقة الكيمياوية

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الخلاصة:

حُضرت نقاط كبريتيد الكادميوم الكمية من أجراء تفاعل كيمياوي بين كادميوم أوليل أمين وبين كبريت أوليل أمين بنسبة مولات 1:6 . تم دراسة الخواص البصرية والطيفية لنقاط الكمية المحضرة . أوضحت النتائج أن الخواص البصرية تعتمد على الحجم البلوري , وكذلك تشكلت مستويات داخل فجوة الطاقة تسمى مستويات القنص .

1. Introduction

A quantum dot is a semiconductor nanostructure that confines the motion of conduction band electrons, valence band holes, or excitons in all three spatial directions [1,2]. The quantum dot have been extensively studied by scientists and engineers over the past few decades because of their unique size dependent optical properties [3].

Many physical properties of nanostructured semiconductors are depend strongly on their size, shape, and crystal structure [4]. Because of their very small size, quantum dot exhibit different optoelectronic behavior than bulk semiconductors of the same composition [3]. In particular, the confined dimensions result in a quantization of the bulk electronic bands and a widening of the gap (called a blue shift) between the valence band and conduction band, which is size dependent [5].

Thus a quantum dot can be seen in analogy to the “particle in a box” model (or “particle in a sphere” model) [6].

The CdS quantum dot is a semiconductor, it's a compound containing an element from periodic table groups II (Cadmium) and groups VI (Sulphur), that have been

extensively used as a light emitting diode (blue emitting device) [7].
CdS has a exciton Bohr radius of 2.8 nm and direct band gap of 2.4 eV and is used in photovoltaics, in light-emitting diodes for flat-panel displays, and in other optical devices based on its nonlinear properties. CdS has been extensively studied during the past few decades [6].

Colloidal Synthesis of Quantum Dots:-

An alternative approach is to produce quantum dots in solutions, called colloidal synthesis, which deals with chemical reactions in solution on a nanometer scale. Colloidal synthesis has been conducted to make semiconductor nanostructures of different composition, size and shapes. This method involves growing nanoparticles of inorganic materials through chemical reaction of

Their precursors and, sometimes, controlled precipitation of the reaction product in certain solvents.

Generally, the growth process starts with the fast formation of a huge number of nuclei. Then more and more of the solid product deposits onto the nuclei, so the sizes of the crystallites grow slowly till the desired size is reached, at which time the reaction must be quenched. Otherwise, the dots could keep growing under a process, known as Ostwald ripening, which is the growth of larger dots through the transfer of material from smaller ones, which have a higher solubility [8].
The methods which used in colloidal synthesis of quantum dot are Thermal evaporation process, and tem plating technique [9].

2. The experimental work

This part represents the description of system which used for preparation of CdS quantum dot. We testing optical properties of the CdS quantum dot by measure the absorption spectrum {by using LABOMED.INC spectra UV/Vis Double Beam cascading , covering range from (190 – 1100) nm} of the well used to calculated the energy gap and crystal size. The emission spectrum of the CdS quantum dot prepared by using VARIAN fluorescence spectrophotometer which supplied from Eclipse Company with the spectrum range from (190-1100) nm. The energy gap and crystal size were also calculated from the emission spectrum.
The samples were tested by using Transmission electron microscope. The structure and calculated the crystal size of the samples by X-ray diffraction (XRD-6000 Labx by Shimadzu X-ray source is Cu source) are included in our study.

System for colloidal CdS quantum dot preparation

a- Three necked round bottle flask were used for the reaction: the first neck for argon gas in and the second for the gas out, and the middle neck (thired) for thermometer, and for adding the reacting compound.
b- Hot plate heater with magnetic stirrer was used for homogenizing the materials.
c- Cylinder for argon gas to flow of argon gas through the reaction was used to expel the oxygen and to prevent oxide formation see figure (1)

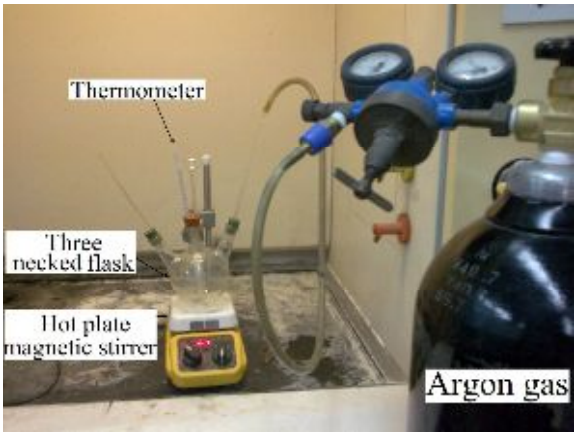


Fig. (1) System for colloidal CdS quantum dot preparation preparation of the solution

The CdS quantum dot was prepared as a colloidal form reaction of cadmium chloride solution and oleylamine (Cd –

oleylamine complex with sulfite oleylamine S- oleylamine).
The explanation of the method is as follows debutante preparation of solution:
Cd-oleylamine complex was prepared (0.6M) by adding 6 mmole of cadmium chloride to 10 ml where the

molarity =mole /volum (liter)

of oleylamine solution (Molecular structure $C_{18}H_{37}N$ supplied by Fluka). The mixture was then transferred to the three-necked flask and argon gas was purged as given before.

The mixture was heated to 90°C with stirring using the magnetic stirrer. After a complete dissolution of the cadmium chloride in oleylamine solution, the mixture was left on a magnetic stirrer for 30 min at 90°C, due to that,the Cd-oleylamine complex was formed.
S-oleyamine solution was first prepared. The best mole ratio for mixing of S-oleylamine: Cd-oleylamine have 6:1mole ratio. Which is the same ratio used by Ken-Tye Yong et al researchers [5]. The molarity of S- oleylamine solution opposite to 0.2M of a Cd–oleylamine complex is 0.6M. The mole ratio was used is the same ratio used [5].

The S- oleylamine of concentration 0.2M was prepared by adding 1 mmole of sulfur to 5ml of oleylamine solution. The mixture was mixed by magnetic stirrer until a complete dissolution, and the colour of the solution was changed from yellow to red, this means that the S- oleylamine was formed.

Synthesis of colloidal CdS quantum dot

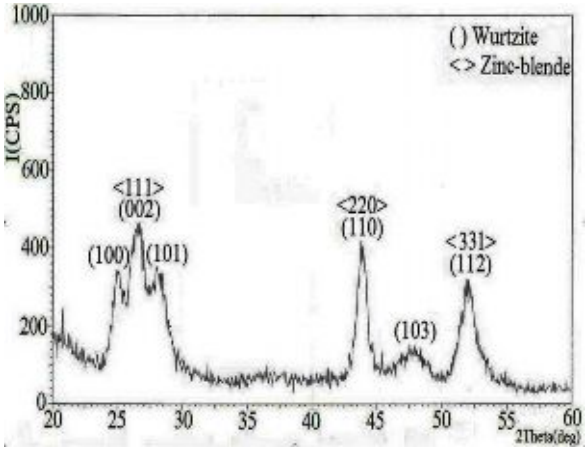
The colloidal CdS quantum dot was prepared by reaction of S- oleylamine solution with Cd- oleylamine complexes. The mole ratio 6:1 was used, and the variation in the mole ratio leads to change in time of formation of dot. Therefore, the time taken is about 3 hours for the mole ratio 6:1 of CdS quantum dot formation as given in the literature [5]:

The Cd- oleylamine complexes solution were heated at 170°C for 20 min under argon flow, and S- oleylamine solution was injected under gentle stirring into the hot reaction mixture.
The reaction mixture was held at 170°C and stirred for 3h, and then aliquot was removed by a syringe and injected into large volume of ethanol at room temperature to quench the reaction. The yellow precipitate of CdS quantum dot formed can be separated by centrifugation [5].
The yellow precipitate at CdS quantum dot was formed and the precipitate dissolved in cyclohexane, toluene, and hexane solvents and tested by emission and absorption spectrum methods. Also the image was taken by electron microscope for CdS quantum dot before the dissolution process.

3. Results and discussion

3-1. X-Ray Diffraction Results for CdS

The X-ray spectrum of the CdS quantum dot prepared is shown in figure (2), for the samples obtained using this method.



Fig(2): The X-ray diffraction for colloidal CdS quantum dot

The X-ray diffraction peaks show that the CdS is formed as compared with the previous X-ray study of the bulk CdS material. The X-ray diffraction for the colloidal shows that X-ray peaks were broad and this result is in good agreement with previous studies [5][10][11][12], which gives an evidence of the nanostructure formation. This is because of

the full width at half maximum (FWHM) of the X-ray diffraction peaks which has a relation with quantum dot size through Scherrer equation.

$$d = \frac{0.9\lambda}{B\cos\theta} \cdot \ldots\ldots \quad (1) \text{ Scherrer equation}$$

d is the quantum dot size.
λ is the wavelength for X-ray source (X-ray source is Cu with λ=1.5406 A°).
B is the FWHM.
θ is the diffraction angle.
From this equation, we can calculate the quantum dot size of the sample prepared. The
results are listed in Table (1).

Table (1) summary of parameters of X-ray diff. and crystal size.

2θ(degree)	FWHM	hkl	Size(nm)
25.1508	1.5	100	5.4
26.5483	1.75	002	4.6
27.998	1.75	101	4.7
43.8720	1	110	7
47.7793	2.75	103	3.1
52.00	1.375	112	6.2

Eventually the average value of the diameter of quantum dot is 5.27 nm.

The optical properties

The absorption spectrum of the CdS quantum dot in colloidal is shown in figures (3).

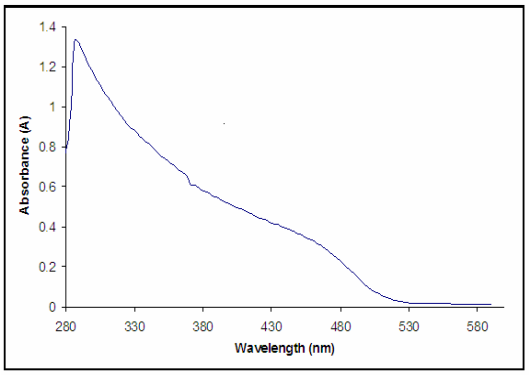


Fig (3): The absorption spectrum for colloidal CdS quantum dot

It can be noticed from this figure that the material absorbs in the region (300-500) nm and transmits in the rest of the visible band. This behavior is the usual characteristics of the CdS material.

The energy gap of prepared CdS quantum dot by chemical methods was calculated form the graphs between $(\alpha h\upsilon)^2$ vs. hυ as in figure (4).

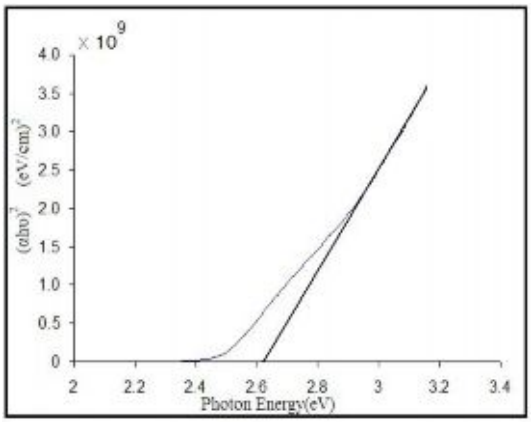


Fig (4): $(\alpha h\upsilon)^2$ vs. photon for colloidal CdS quantum dot

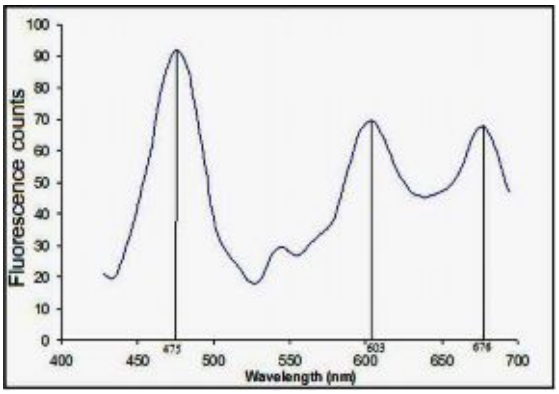
The values of energy gap calculated from figure (4) is equal 2.63 eV. The relationship between the energy gap and crystal size is given by equation (2) [6].

$$\Delta E = \frac{\pi^2 \hbar^2}{2 m^* e R^2} \ldots\ldots\ldots \ldots (2)$$

$\Delta E = Eg_{dot} - Eg_{bulk}$
Where Eg_{dot} is quantum dot band gap
Eg_{bulk} is bulk band gap
Eg_{bulk} = 2.42 eV
$Eg_{q.dot}$ = 2.63 eV
R is quantum dot radius
e is charge electron
m* is effective mass of crystal (1.82×10^{-31} kg for CdS)
By substitutes the above values in eq(2) , the crystal size about 6nm.

These expansions in the energy gap give more evidence for the formation of the CdS quantum dot in the colloidal synthesis.

The fluorescence spectrum of the quantum dots formed by the colloidal synthesis is show in figure (5).



Fig(5): The fluorescence spectrum for colloidal CdS quantum dot

The figure shows that the band edge transmission is catered equal (475) nm indicating a energy gap of (2.67) eV by using equation (3).

$E(eV) = 1240/\lambda(nm)$……(3)

Using equation (1) the diameter for CdS quantum dot yield were (6.29) nm.

There are two peaks around (603 and 676) nm in figure (5), These two peaks due to the emission from the trap state which are generated by the nanostructure and established the allowed transition states in the band gap.

The trap states are in energy of (2 and 1.83) eV can see that in figure (6).

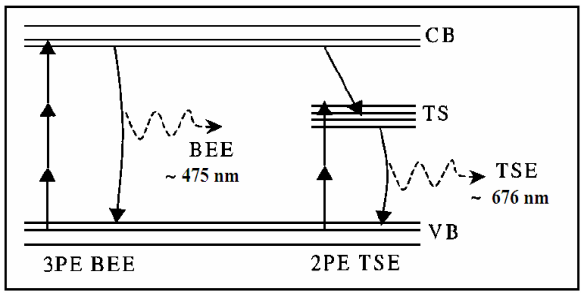


Fig (6) photon excited emission spectra of CdS quantum dot [13]

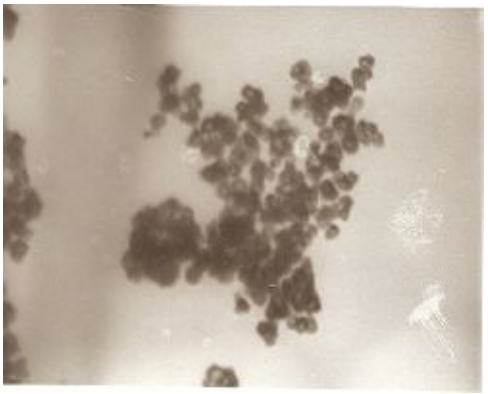
Where (BEE) is the band edge emission, (TS) is the trap state, (TSE) is the trap state emission.

These two bands are originated from the defect state in the energy band.

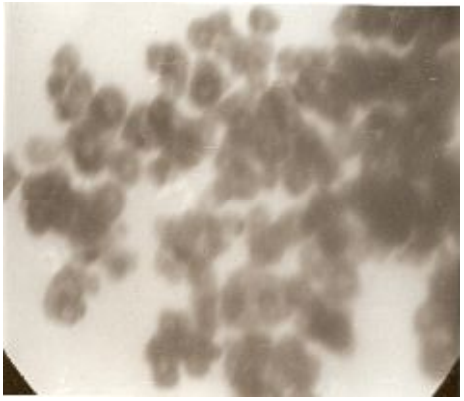
These peaks are usually considered as a good indication for the nanostructure and the quantum dot formation [13].

3-2. CdS quantum dot morphology study by transmission electron microscope

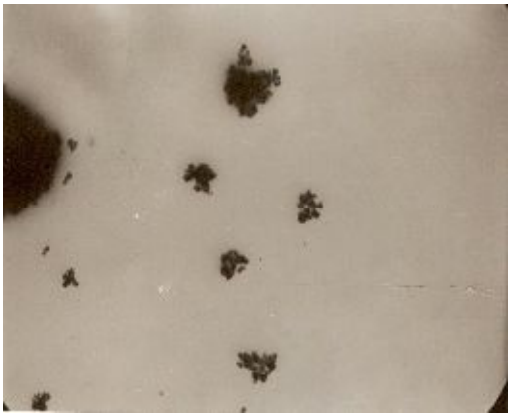
The images of the prepaned sample were viewed by the transmission electron microscope (TEM) which is shown in figures (7a,7b,7c).The image shows that a quantum dot was formed in demission order of 4-6nm.



Fig(7a): (TEM) images for colloidal CdS quantum dot,The scale bar ~ 230nm



Fig(7b): (TEM) images for colloidal CdS quantum dot, The scale bar ~ 90nm



Fig(7c): (TEM) images for colloidal CdS quantum dot, The scale bar ~ 320nm

Conclusion:

The chemical reaction of the Cd-oleyamine and S- oleyamine solution was formed to be a good technique to prepare the CdS quantum dots. The add of oleyamine make the probability of formation of the CdS quantum dots is very high with dimension in order of 4-6 nm.

The optical properties of the product quantum dots were tested to gives the evidence of quantum dots formation by the above method. It was found that the energy gap was varied with the dot dimension.

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