Effect of pyridine and pyridine with substituent on the optoelectronic spectrum of nanoparticles CdS prepared by liquid – liquid interface reaction

Salma M. Shaban, K. T. Al-Rasoul, A. S. Ahmed

Abstract— CdS nanoparticles are prepared by using liquid – liquid interface reaction. from the XRD and TEM analysis we estimated that the size of particles is about 5 nm , which is very comparable with Bohr radius of the CdS (a_B 3 nm) . The surface are treated through Immersion the powder of nanoparticles on the solution with mix ratio from pyridine and methanol (1:9) for one hour, then the study the UV-Visible spectrum of the solution. The results indicate a blue shift according to the decrease in the size.

Keywords — CBD, Liquid-Liquid Interface, Nanoparticles.

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1 INTRODUCTION

THe relation between the surface chemistry and the electronic properties in semiconductor play a main role when we want to constructed the semiconductor devices, and for nanoparticles growth the solubility and prevent of aggregation of particles can be satisfy through the organic legend which exist in the end of the surface. in the currently research we can notice that there is a big amount of interest about the controlling the electronic properties of nanoparticles semiconductor through the use of surface ligands and through the chemical method. A molecules can reacted onto surface of semiconductor and this give us ability to tune the transport of charge carrier [1,2]. It has been found that the nature of ligand layer surrounding semiconductor nanostructure strongly effects on the opto-electronic properties [3].

Pyridine is an aromatic compound with nucleophileic substitutions [4], the substituent with pyridine can be divided into two group, the electron donating group EDG which add electron density to the π system making it more nucleophilic and the electron withdrawing group EWG which remove electron density from the π system making it less nucleophilic that describes the affinity of a nucleophile to the nuclei. And note that the Electron-donor groups in the ring increase the reactivity of the N-atom towards electrophiles and the Electron-acceptor groups decrease the N-atom reactivity towards electrophiles. In our work, are used the following from pyridine family [4] Pyridine , 2-methlypyridine (2-picoline) , 4-methlypyridine (4-picoline) , 2-methoxypyridine ,3-idopyridine , 4-idopyridine ,4-ethlypyridine. Table 1 gives some properties of the previous material. Also is studied the effect of pyridine and pyridine with substituent on the opto-electronic spectrum of nanoparticles CdS prepared through the super saturation using liquid –liquid interface reaction method.

2 EXPERIMENTAL PART

2.1 Method of Preparation

The method to prepare nanoparticles CdS by using liquid – liquid interface reaction need to pass through two steps, the first step is to prepare the precursor which acts as the source of the Cadmium and the second step is the reaction at the interface between two immiscible liquid to get a nanoparticle CdS. So in the first step to get the precursor cadmiumdiethyl-dithiocarbamate, we applied the procedure that describe by O'Brien and R.Nomura [5]. In this procedure we dissolve (11 mM) from Sodium hydroxide in 50 ml methanol using a magnetic stirrer. Then we added (1.128 ml) diethlamine and (0.65 ml) Carbon disulfide. We note that the solution has a pale yellow. After that and by using the ice bath cooled the solution to 40C for eight hour then added by dropping wisely 50 ml of the methanol which dissolve in it (5.5 mM) from Cadmium Chloride and take it under stirrer for one hour and then note a yellow solid which represent to produce the precursor then filtered and wished by methanol.

then by water and at the last with methanol then dry it by oven in the temperature (650-700 c) for 12 hour. In the Second step, worked to prepare the nanoparticles CdS by apply the following steps: at the first dissolve Na_2S in deionized water (11.46 mg .0.147 mmol) which consider as the source of sulfide .then added above it 50 ml of toluene containing 30 mg (0.073 mmol.) of cadmium diethyldithiocarbamate. Now noticed two immiscible liquid one above each other and separated by interface layer as shown in the Fig. [1], then put the beaker into an oven held at 650 C and left it.undisturbed for 24 hour . Att end of this time, a yellow thin film was found adhered to the interface of the two liquids.

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then left it for one houre ,then measure the UV-Visible absorbance of the solution .

3. RESULTS AND DISCUSSION

3.1 Analysis of X-ray Diffraction Pattern

From the X-ray diffraction pattern for nanoparticles CdS without any surfactant added, which obtain in Fig. 2, note that we have peaks at 2θ can be assigned to [002], [110], [112] planes of hexagonal CdS. And can note that the peak at 2θ=25.590, 2θ=42.50, and 2θ=51.130 attributed to the [002] for hexagonal structure or [111] for cubic, the [110] for hexagonal structure or [220] for cubic the [112] for hexagonal structure or [311] for cubic respectively. But the peak at 24.930 are purely indicate to [100] for hexagonal structure. we consider that the deposited consists of both the cubic and hexagonal forms. Such mixed phases have been previously reported in chemically deposited CdS nanostructures [6-10]. And note that the producer is free from crystalline impurities.
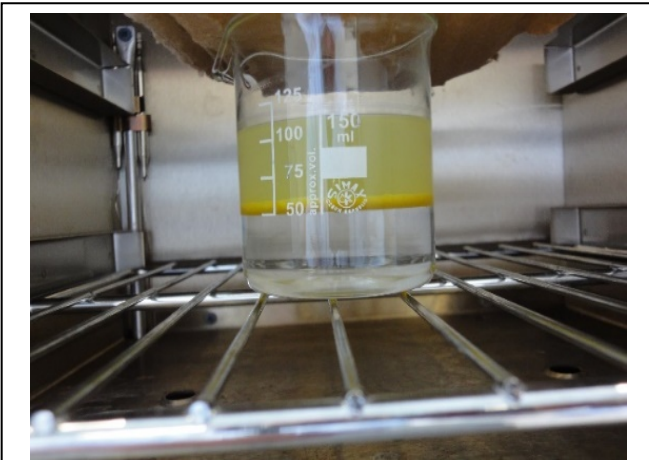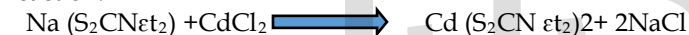

Fig. 1. Two immiscible liquids to get the interface reaction for nanoparticles CdS.

2.2 Procedure of Preparation

The procedure of the previous steps can be explain in the following equation:

$NaOH + CS_2 + HN\varepsilon t_2 \longrightarrow Na (S_2CN \varepsilon t_2) + H_2O$

After cooling added Cadmium Chloride and get the following reaction:

$Na (S_2CN\varepsilon t_2) + CdCl_2 \longrightarrow Cd (S_2CN \varepsilon t_2)2 + 2NaCl$
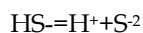
In this step, get the precursor Cd $(S2CNEt2)2$ which can be used in the following steps to produce nanoparticle CdS as:
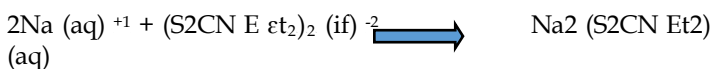At the first we dissolved Na2S in deionized water as shown in the following equation:

$Na_2S + H_2O = NaOH + H_2S$
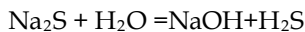
Then H₂S dissociated according to the following equation :

$H_2S = H^+ + HS$
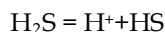
And at last HS dissociated as in the equation

$HS- = H^+ + S^{-2}$

All these done in an aqueous solution for Na₂S, so the last result is the H^+ and S^{-2} when layered the toluene above the aqueous solution which contain the Cd $(S_2CN \varepsilon t_2)_2$. The following reaction act in the interfacial layer which separated the two solutions

$(S_2CN \varepsilon t_2)_2 (if) + S^{-2}(if) \longrightarrow CdS(if) + (S_2CN \varepsilon t_2)2-2(ol)$

$2Na (aq)^{+1} + (S2CN E \varepsilon t_2)_2 (if)^{-2} \longrightarrow Na2 (S2CN Et2)$ (aq)

2.2 Procedure for Surfactant

Immerse 0.1 gm from powder of nanoparticles CdS in the solution which consist of 1 ml of pyridine in 9ml of methanol ,
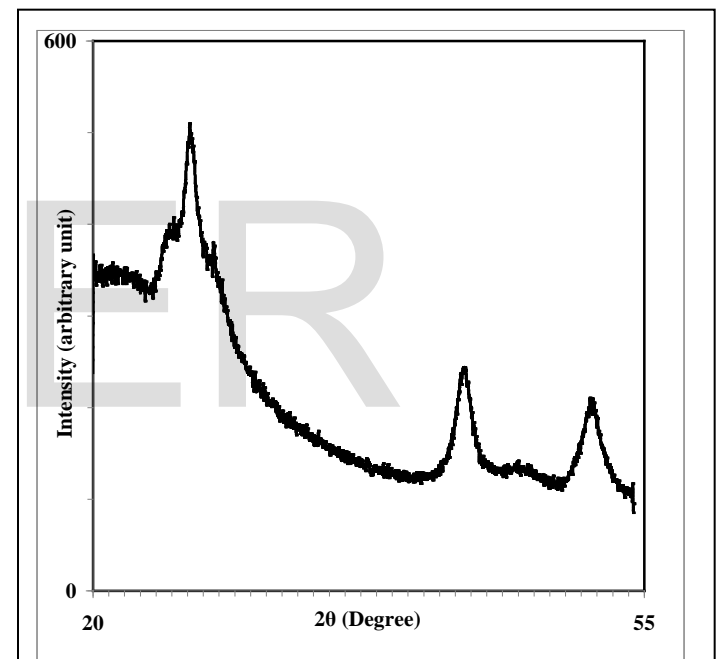

Fig. 2. X-ray diffraction patterns obtained for nanoparticles CdS using the interface reaction for the system of H2O – Toluene.

TABLE1
THE PARAMETERS FROM X-RAY DIFFRACTION PATTERN

2θ (Deg.)	d_{hkl} Exp.(Å)	d_{hkl} Std.(Å)	phase	hkl	card No.
24.93	3.5688	3.5808	Hex.	(100)	96-900-8863
25.59	3.4782	3.3745	Hex.	(002)	96-900-8863
		3.3544	Cubic	(111)	96-101-1252
42.50	2.1253	2.0674	Hex.	(110)	96-900-8863
		2.0541	Cubic	(220)	96-101-1252
52.13	1.7531	1.7629	Hex.	(112)	96-900-8863
		1.7518	Cubic	(311)	96-101-1252

The broadening of the peaks indicating that we have a nanoscale of the size. The grain size of the particulates can be estimated using Scherer equation:

$$d = 0.9 \, \lambda \, / \, \beta \cos \theta \qquad (1)$$

Where β is the full width at half maximum in radians, λ is the wavelength of X-ray used and θ the angle of diffraction. And when apply this relation for the diffraction angle in Fig. 2, get that the average size of grains was equal to 7.73 nm and

TABLE2
VALUES OF GRAINS SIZE FROM X-RAY DIFFRACTION PATTERN

2θ (degree)	Observed FWHM (degree)	Grain size (nm)
25.59	1.1949	7.6
42.5	1.0584	8.9
52.13	1.6482	5.9

when are compare with Bohr radius we note that it is in the range of nanoparticle (two or three multiple of Bohr radius or in the range (2-10) nm. Table 2 indicates the calculation of value of grains size using Scherer equation.

For actual size of grains, the broading of the peaks may be caused by residual stresses. Stresses within the crystal cause corresponding strains, which result in a planar spacing and shifting the peaks. Often residual stresses produce a combination of compressive and tensile strains. In order to calculate the average crystallite size including strain, adopted the Williamson –Hall method [11,12] where the strain (ε) and crystallite size (L) are related to the measured β following the equation:

$$\beta \cos \theta \, / \, \lambda = 1/L + \varepsilon \, \sin \theta \, / \, \lambda \qquad (2)$$

Where β, λ and θ are the full-width at half maximum (FWHM) of the diffraction peaks, wavelength of the x-ray source and Bragg's angle respectively. For this calculation, the most prominent peaks as shown in the inset of Fig. 2 were analyzed. Fig. 3 represents the plot of (β cos θ / λ) versus sin θ / λ which is a straight line. The slope of the plot gives the amount of residual strain, whereas reciprocal of intercept on the y-axis give the average particle size. Values 1.56×10^{-2} and 10.4 nm are obtained for strain and average grain size, respectively.
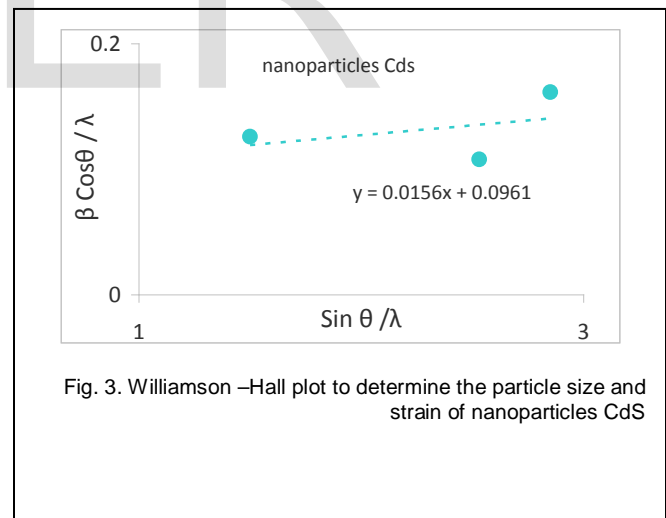

Fig. 3. Williamson –Hall plot to determine the particle size and strain of nanoparticles CdS

imum (FWHM) are obtained using the first derivative of the curve as shown in Fig. 5

TABLE3
Value of ($\beta \cos \theta / \lambda$) and ($\sin \theta / \lambda$) to apply Williamson –Hall method

2θ	β deg	β Rad	λ nm	$\sin \theta / \lambda$	$\beta \cos \theta / \lambda$
26.5^0	1.1459	0.01998	0.15406	1.5	0.126
43.6^0	1.0306	0.01797	0.15406	2.53	0.108
51.9^0	1.5872	0.02768	0.15406	2.85	0.1615

3.2 Transmission Electron Microscopy

Transmission electron microscopy gives us more detailed about the structure. From the picture that results from transmission electron microscopic, notice that the Individual grains making up the platelets can clearly resolved, especially at high resolution. Lattice fringes corresponding to the spacing between (110) and (002) planes of hexagonal CdS are clearly seen in figure 4. The long edge of grains is typically around 3 nm.
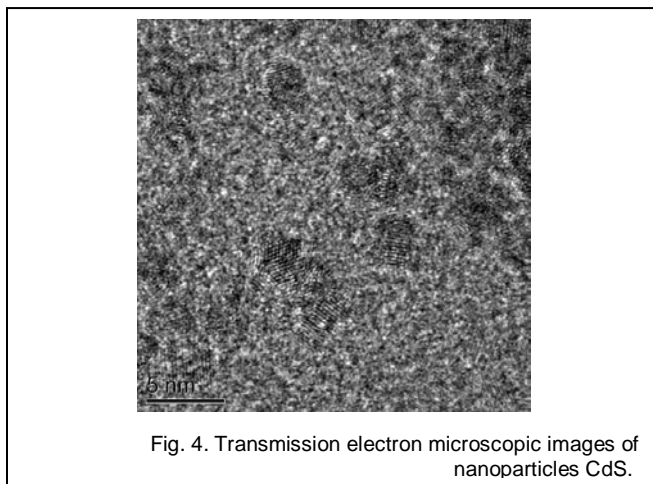

Fig. 4. Transmission electron microscopic images of nanoparticles CdS.

3.3 UV-Visible spectrum analysis

To estimate the energy gap and the size can be used tight binding approximate (gaussing fitting). This is model was derivative by D.D Sarma and co-workers which is used to calculate of band gap of colloidal sols [13,14]. To apply this method, the position of peak (E0) , as well as its full width at half max-
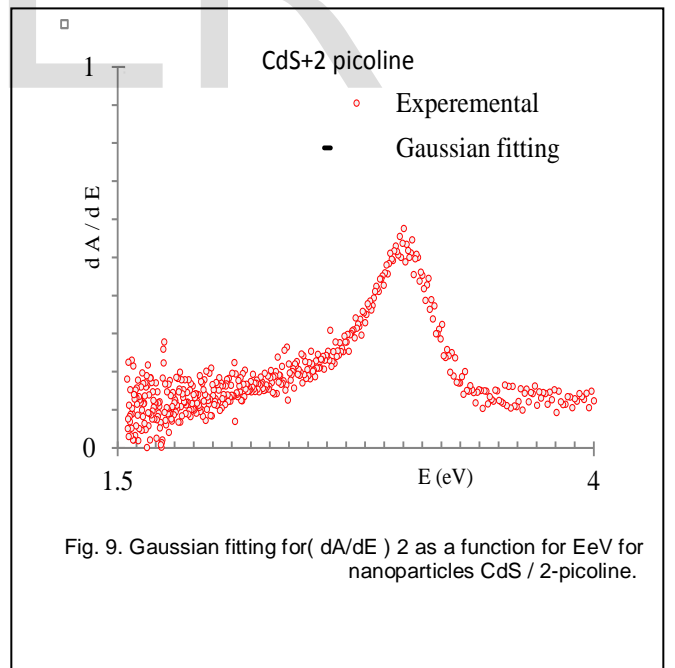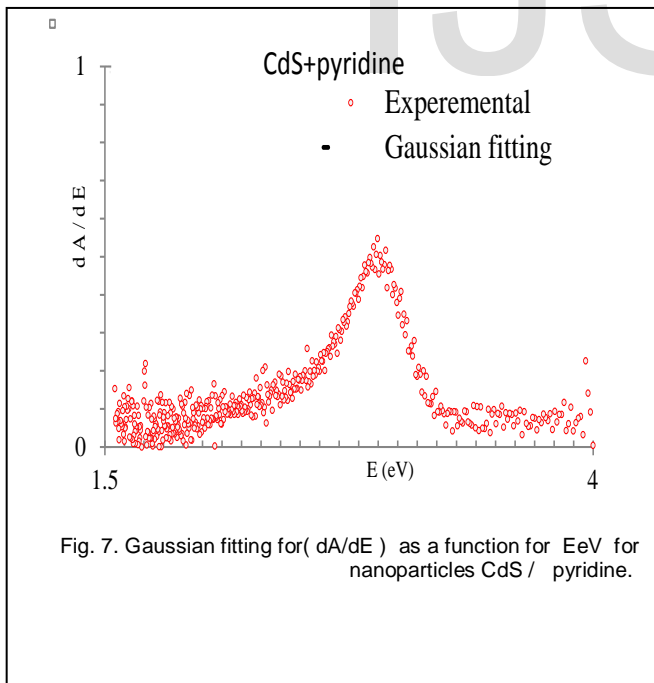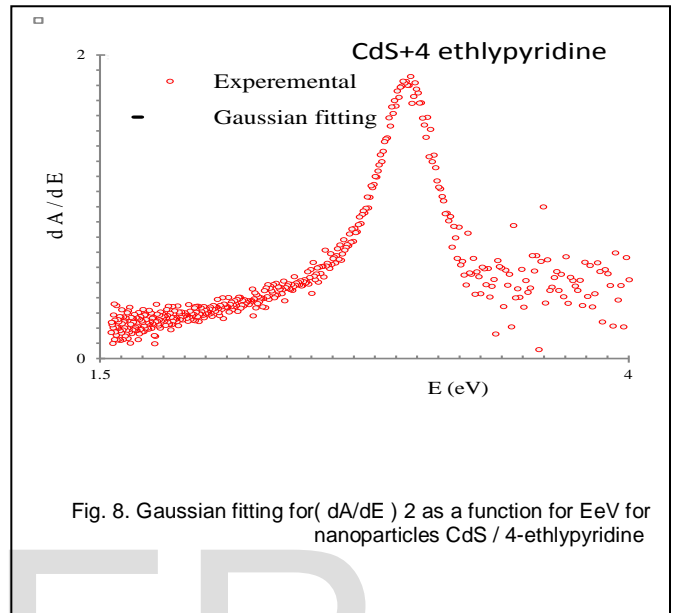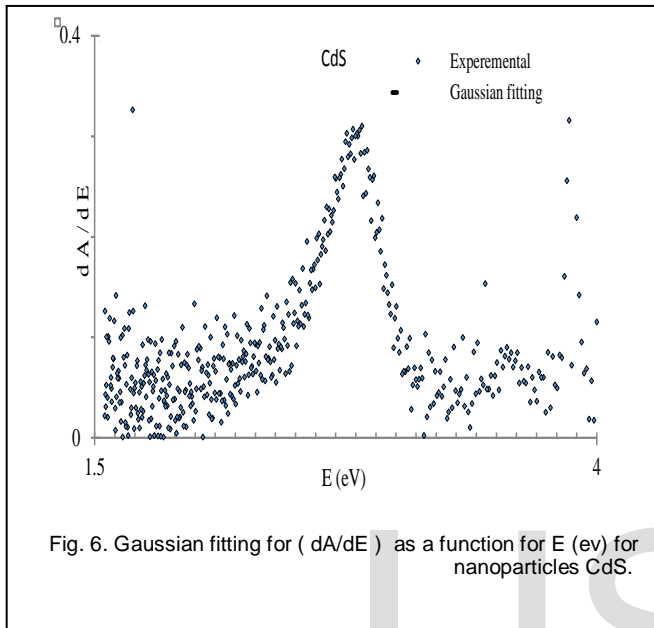

Fig. 5. Exhibits: (a) Electronic absorption spectrum of CdS nanocrystalline thin film, (b) Gaussian fitting of the spectra the CdS nanocrystalline thin film [7].

The UV absorption spectrum for CdS is shown in Fig. 6a. Differentiation of this absorption spectrum yields the curve shown in Fig. 6b. In order to obtain the position of absorption maxima, Gaussian function fitting of absorption spectra was performed, as shown in Fig. 6b. To apply this method, the position of the peak energy E0 is obtained using the first derivation of the curve. The E0 is translated as d [5-8] by usiing the formula

$$\Delta E_g = 1/ad^2 + bd + c \qquad (4)$$

Where a, b and c are constants that depend on the identity of the semiconductor; for CdS their values are 0.1278, 0.1018 and 0.1821 respectively. Here, ΔE_g is the observed shift in the band gap (Eg) given by E0 – Eg..

Fig. 6. Gaussian fitting for (dA/dE) as a function for E (ev) for nanoparticles CdS.

Fig. 8. Gaussian fitting for(dA/dE) 2 as a function for EeV for nanoparticles CdS / 4-ethlypyridine

Fig. 7. Gaussian fitting for(dA/dE) as a function for EeV for nanoparticles CdS / pyridine.

Fig. 9. Gaussian fitting for(dA/dE) 2 as a function for EeV for nanoparticles CdS / 2-picoline.
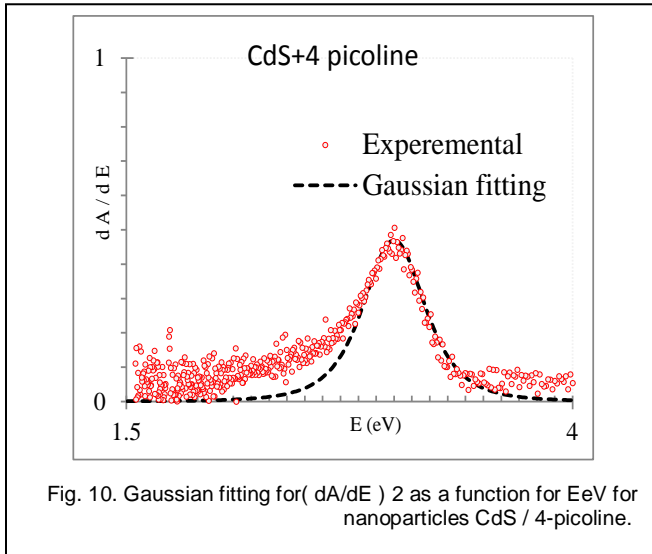
Fig. 10. Gaussian fitting for(dA/dE) 2 as a function for EeV for nanoparticles CdS / 4-picoline.
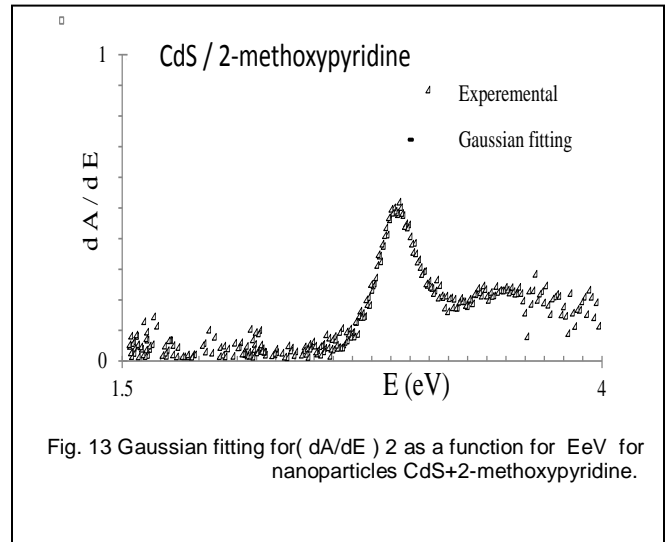

Fig. 13 Gaussian fitting for(dA/dE) 2 as a function for EeV for nanoparticles CdS+2-methoxypyridine.
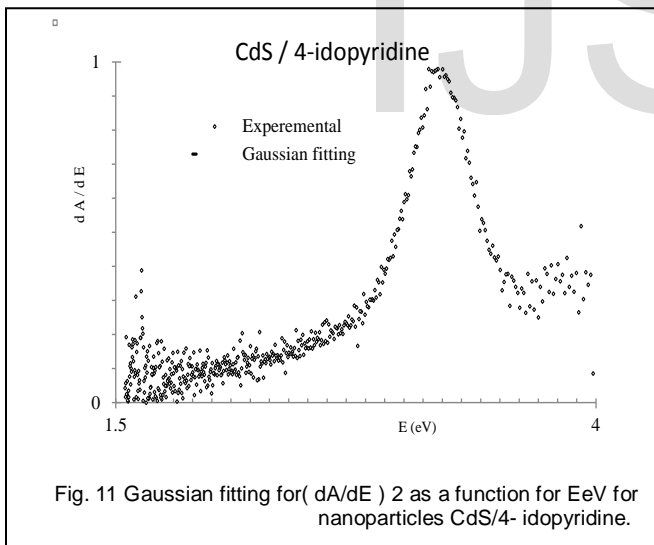

Fig. 11 Gaussian fitting for(dA/dE) 2 as a function for EeV for nanoparticles CdS/4- idopyridine.
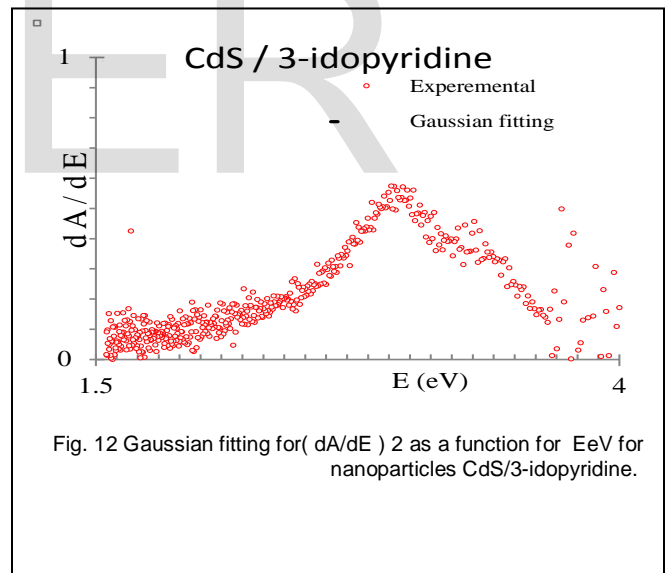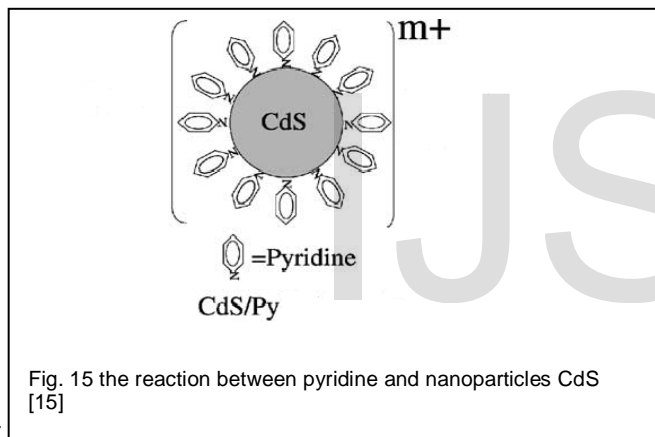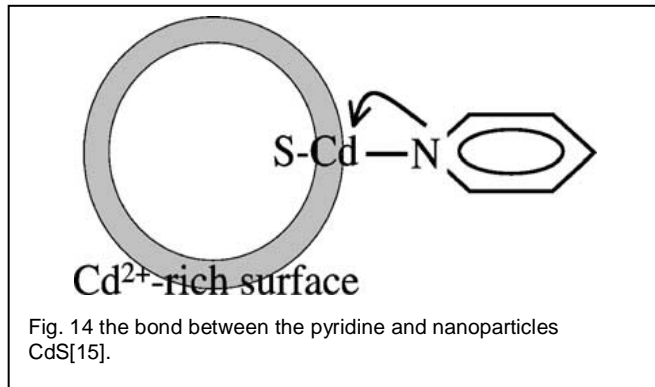

Fig. 12 Gaussian fitting for(dA/dE) 2 as a function for EeV for nanoparticles CdS/3-idopyridine.

We must know that for nanoparticles CdS after reacted with pyridine , this indicate that the nitrogen atom in pyridine is nucleophilic because the lone pair of electrons on nitrogen cannot be delocalized around the ring. For CdS nanoparticles whose structure is similar to a strong electrolyte have Cd^{+2} rich surface is capped and bound to surface by the electrically neutral ligand pyridine as shown in the figure.[14,15]

Fig. 14 the bond between the pyridine and nanoparticles CdS[15].

Fig. 15 the reaction between pyridine and nanoparticles CdS [15]

From Table 4, the Pka value relates to electron density of nitrogen atom in the pyridine ring [16] and this represent to strength of reaction with nanoparticles, so when pyridine reacted with nanoparticles it reacted with surface of these particles and this make surrounding layer insulator for these particles from others and prevent them to aggregation, so at the first, notes that the energy gap of all samples increase which represent to the decrease in size and then depend on the Pka to note amount of this change , so when substituent belong to the electron donating group we notice that the change in band gap is small and decrease with the increase the pka which may be means that the ability to aggregation depend on the electron density of nitrogen atom , on the other hand, notice that the band increase with decrease the Pka of the substituent when belong to the electron with drawls group and this may returns to the reduce of electron density of nitrogen on the acclamation of particles.

TABLE4

THE PYRIDINE AND PYRIDINE WITH SUBSTITUENT EFFECT ON THE NANOPARTICLES CdS

ΔPka ($Pka_{pyridine} - Pka_{pyridine\ +substituent}$)	Effect of substituent on the pyridine ring	Eg (eV)	d (nm)
------	------	2.8	3.9
positive	EDG	3.05	2.9
positive	EDG	3	3
positive	EDG	2.95	3.2
0	-----	2.9	3.4
negative	EWG	3.2	2.5
negative	EWG	2.95	3.2
negative	EWG	2.9	3.4

4. CONCLUSIONS

nanoparticles CdS prepared using liquid -liquid interface reaction , the size is comparable to the Bohr radius of CdS , and this estimated through XRD , TEM , and UV-Visible analysis. for estimated the nanosize and the energy gap from UV-Visible spectrum we use the model that derivative by Samara at el. which give us much accurate result . in our work we aim to study the effect of pyridine and pyridine with substituen familly on the opto-electronic spectrum of the nanoparticles CdS through the reacted with the surface of these particles , and we reach that there is an increase in the energy gap for all samples which mean that there is a change in the size according to the substituen in the pyridine ring . and we reach this chang depend on the electron density on the niterogen atom in the pyridine ring and this density of electron can be estimated from Pka value.

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