Synthesis, Structural and Optical Properties of Cds Nano-particles Prepared by Chemical Method

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ABSTRACT

In this work, CdS nanoparticles were synthesized via chemical method using thioacetamide (TA). X- ray diffraction (XRD), Atomic force microscopy (AFM) and UV-VIS transmission spectroscopy were employed to characterize the size, morphology, crystalline structure and optical properties of the prepared material. X-ray diffraction analysis confirms the formation of cubical and hexagonal structures of CdS nanoparticle with average particle size (3.2nm). AFM show the formation of aggregate of nanoparticle with particle size ranging 7 – 20 (nm). From the shift in optical band gap, particles size can be calculated using Effective mass approximation (EMA) was (2.3nm), and found a good agreement with those determined from XRD broadening, while AFM show higher particle size due to aggregation of nanoparticles.

Keywords: CdS nanoparticles, quantum dot, chemical synthesis, optical properties, structure properties.

الخصائص التركيبيه والنبوية والبصريه و لجسيماتCdS النانويه المحضره بطريقه كيميائيه

الخلاصة

في هذا العمل، حضرت جسيمات نانويه من CdS بطريقة كيميائيه وباستخدام (TA) thioacetamide. استخدم حيود الاشعه السينية (XRD)و مجهر القوة الذريه(AFM) و مطياف النفاذيه للاشعه المرئيه - فوق البنفسجيه (UV-VIS) لتحديد الحجم وطبيعه السطح و التركيب البلوري والخصائص البصريه للماده المحضره . يبين تحليل الاشعه السينيه تكوين تراكيب مكعبه وسداسيه للجسيمات النانويه من CdS مع معدل حجم جسيم(3.2nm) . يوضح(AFM) تشكيل مجاميع للجسيمات النانويه مع حجم جسيم يتراوح بين (nm) 20 – 7 . من الازاحه في فجوه الطاقه البصريه، يمكن حساب حجم الجسيم باستخدام تقريب الكتله الفعالة (EMA) وكان (2.3nm)وتبين توافق جيد مع تلك المحدده من اتساع XRD ، بينما يوضح AFM اعلى حجم جسيمات نتيجه تكتل الجسيمات النانويه.

INTRODUCTION

Nanoparticles constitute a major class of nanomaterials. Nanoparticles are zero-dimensional, possessing nanometric dimensions in all the three dimensions. The diameters of nanoparticles can vary anywhere between one and a few hundreds of nanometers. Small nanoparticles with diameters of a few nanometers are comparable to molecules [1] Nanoparticles are of great scientific interest because they exhibit unique electronic, optical and photonic properties and are an ideal size for use as nanotechnological building blocks. They may be composed of any substance, including metals, semiconductors, core- shell composite architectures, and organic polymers. These particles often display properties intermediate between quantum and bulk materials because of their intermediate size and surface area to volume ratios [2]. Nanoparticle with exciton Bohr diameter exhibits a blue shift in the exciton energy, which is the so-called quantum size effect. It is explained that the continuous energy band of the bulk crystal transforms into a series of discrete energy states resulting in the broadening of the band gap due to the finite size of the nanoparticle. Brus [3] proposed the effective mass approximation formula (EMA) to explain the theory of blue shift, which gives energy ***E(R)*** for the lowest direct interband transition energy as a function of nanoparticle radius ***R***, shown as follows:

$$E(R) = E_0 + \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8\,e^2}{\epsilon_2 R} + \frac{e^2}{R}\overline{\sum_{n=1}^{\infty}\alpha_n\left(\frac{S}{R}\right)^{2n}} \quad \text{-------- (1)}$$

Where E_0 is the band gap in the bulk form, m_e and m_h are the effective mass of electrons and holes respectively, e the electronic charge. ε the dielectric constant of the medium , α_n is a function of dielectric constant and S is the electron- hole separation. The second term in the right hand side of the above equation represents the quantum localization energy. The third and fourth terms correspond to the Coulomb potential and polarization energy respectively.

II–VI semiconductors nanoparticles attract more attention because of their easy synthesis in the required size range. CdS is one of very important II–VI direct band gap semiconductor; among the II–VI semiconductor compounds, CdS is a promising material because of their applications in optoelectronics [4], photo catalysts [5], solar cell [6] and nonlinear optical material [7].

CdS Nanoparticles have been synthesized by a variety of methods including a sol-gel template [8], microwave - solvothermal route [9], hydrothermal reaction [10], laser ablation [11], chemical bath deposition [12] and chemical method [13, 14]. Chemical method is a simple, clean and inexpensive technique to obtain CdS nanoparticles. Nanoparticles was obtained by thermal decomposition of thioacetamide (TA) in an acid solution of Cadmium nitrate creates the supersaturating condition necessary to CdS homogenous precipitation. Here, report a details study on structure and optical

properties of CdS nanoparticles produced by thermal decomposition thioacetamide (TA).

Experimental procedure

CdS nanoparticles were synthesized via chemical method. 1.1g of cadmium nitrate $Cd(NO_3)_2.4H_2O$ were dissolved in 250mL distilled water, containing 0.2M of nitric acid. Then 0.57g of thioacetamide (TA) was added. The solution was then immersed in a water bath at the reaction temperature of 80°C, after a certain period (30min) of aging a yellow in the solution was judged to indicate the onset of precipitation. The precipitate was allowed to evaporate at room temperature for 18h to obtain CdS nanoparticles in yellow powder form. This powder was characterized by XRD pattern. A small portion of powder dispersed in DMSO (dimethyl sulphoxide) and ultrasonically was used to record UV-VIS transmission spectrum.

In principle, the chemical process involves reacting Cadmium nitrate solution with thioacetamide (C_2H_5SN) (TA), which decomposed in acidic environment and releases Sulfide ions. The sequence of chemical processes involved in the formation of CdS nanoparticles as follows:

$$Cd(NO_3)_2.4H_2O \rightarrow Cd^{2+} + 2NO_3^- + 4H_2O$$

$$CH_2H_5SN + HNO_3 \rightarrow S^{2-} + 2H^+ + by\ products$$

$$Cd^{2+} + S^{2-} \rightarrow nan\ CdS$$

The structure characterization and average particle size of CdS nanoparticles were performed by X- ray diffractometer (Philips, PW/1710), with monochromatised CuKα radiation of wavelength 0.15418nm at 40KV and 30mA. The peak profile record corrected full-width at half maximum (FWHM) and accurate crystallite sizes were determined from the x-ray diffraction data using the Debye Scherer's formula ($G= 0.9 \lambda / D \cos\theta$), where G is the particle size, D is the full width at half maximum, λ is the wavelength of X-ray and θ is the Braggs reflection angle of x-ray beam. A UV-VIS transmission spectrum was recorded employing a Cecile-7200 double beam UV/VIS spectrophotometer supplied by Aquarius Company for the wavelength range of 200-900 nm. The surface morphology and particle size were characterized using Atomic force microscopy (Advance angstrom Inc. SPM AA3000).

RESULT AND DISCUSSION

X-ray diffraction Results

Figure (1)shows the X-ray diffraction pattern of the CdS nanoparticles, XRD peaks were found at 2θ values of 26.5°, 44° and 52°, referring to diffraction from (002), (110) and (112) planes, reflections of the hexagonal modification or (111), (220) and (311) reflection of the cubical zinc blend CdS. Also there were shoulders around 25° and 28.3° corresponding to the hexagonal phase in the XRD spectrum[14,15]. Therefore,

as-prepared sample is mixtures of cubical and hexagonal phases; Table (1) shows the obtained result of X-ray diffraction pattern. The broadening of diffraction peak provides information about average particle size. The average particle size was calculated using Debye Scherrer's formula. Corresponding to the maximum intensity peak ($2\theta = 26.5^{o}$) particle size was 3.2nm. It is experimentally observed that broadening arising from the small crystallite size differs from the broadening due to strained crystals.

Optical properties

Figure (2) explain the transmission spectrum on CdS nanoparticles, from figure can notice that transmission (T%) reach to 2.5 at short wavelength and this attribute to high absorption of nanoparticles at these wavelength, then the transmission increased as s wavelength increased [16]. It is also observed from spectra a blue shift in band edge (~440nm) as compared to bulk CdS absorption edge (512nm), the amount of blue shift is (82nm). The main reasons for the blue shift are the quantum dimensional effect of the nanoparticles, which induce the wider band gap and the blue shift of the absorption band due to the decrease of particle size, and the surface effect of the nanoparticles, because the large surface force will cause crystal lattice aberration and a small crystal constant. At the same time, the short band length will induce the increase of the bond intrinsic oscillation frequency of nanoparticles, leading the blue shift of the absorption band. Therefore, the nanoparticles size is smaller and the blue shift is more obvious [10]. These result was agreement with Bhattacharya [13] which obtained (47nm) blue shift and Singh[14] obtained (84nm) blue shift. From the transmission data, nearly at the fundamental absorption edge, the values of absorption coefficient α are calculated in the region of strong absorption using the following equation [17]:

$$\alpha = \frac{1}{t} In \left(\frac{1}{T}\right) \qquad \text{-------- (2)}$$

Where t is the thickness and T transmission. The energy gaps E_g of CdS nanoparticles was estimated using Tauc relation [14]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \qquad \text{---------- (3)}$$

Where α is the absorption coefficient, Eg is the band gap energy, A is constant $h\nu$ is the photon energy. The band gap was determined from figure (3), which shows a plot of $(\alpha h\nu)^2$ versus $h\nu$ for CdS nanoparticles the intercept of the straight line with the $h\nu$ axis gives the band gap E_g, which is 2.85 eV due to quantum confinement. The band gap energy is inversely proportional to the square of the particle radius R [14]. Also, the extinction coefficient k can be calculated by the following equation [17]:

$$K = \frac{\alpha \lambda}{4\pi} \qquad \text{---------- (4)}$$

Figure (4) shows the variation of absorption coefficient α with wavelength for CdS nanoparticles. Notice that the nanoparticles have high absorption coefficient in short wavelength and this will be decrease at long wavelength where the nanoparticles become transparent in this region. While Figure (5) show the variation of extinction coefficient with wavelength, excitation coefficient related to attenuation value of electromagnetic wave where its passed through the medium, so that the high value of short wavelength related to the loss incident energy in absorption process or due to loss the wave in electron transit between the energy level but this result is revere in long wavelength this is may be related to appear another absorption process such as absorption by charge carrier. Also excitation coefficient of nanoparticles was higher than for bulk CdS, this may be attributed to the substantial increase in the oscillator strength due to the quantum confinement of CdS nanoparticles [18].

EMA approximation calculation

In the effective mass approximation EMA, can use the energy position to estimate the average particle size. According to equation (1), the Coulomb potential and polarization energy were small compared to electron- hole confinement kinetic energy, so that this equation can be written as:

$$E(R) = E_0 + \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) \text{---- (5)}$$

Where E_0 = 2.42 eV, m_e=0.21m_o, m_h=0.80m_o, and m_o is the free electron mass[14], so that the particle size obtain is 2.3nm.

AFM

Figure (6) shows the AFM images of CdS nanoparticles (image size 1000nm x 1000nm). Upon inspection of the image in the AFM measuring system, it is observed that the Root mean square (RMS) is 0.152nm. The histogram of size distribution of CdS nanoparticles (figure (6) b) shows particle size ranging from 7-20 nm. In comparison, the particles size of CdS nanoparticles analyzed by AFM is higher than that by XRD and EMA. This difference is due to the formation of large aggregates of CdS nanoparticle [18].

CONCLUSIONS

CdS nanoparticles were synthesized via chemical method using thioacetamide (TA) method; the XRD pattern of CdS nanoparticles showed the materials to be at the nanometeric size regime with hexagonal and cubic phase structure. Also particle size of CdS nanoparticles was obtained from UV- VIS transmission spectra by using EMA. The dispersion spectra of α and *k* obtained from the transmission data. While, AFM shows particle size are in the range of 7-20 nm with RMS about 0.152nm.

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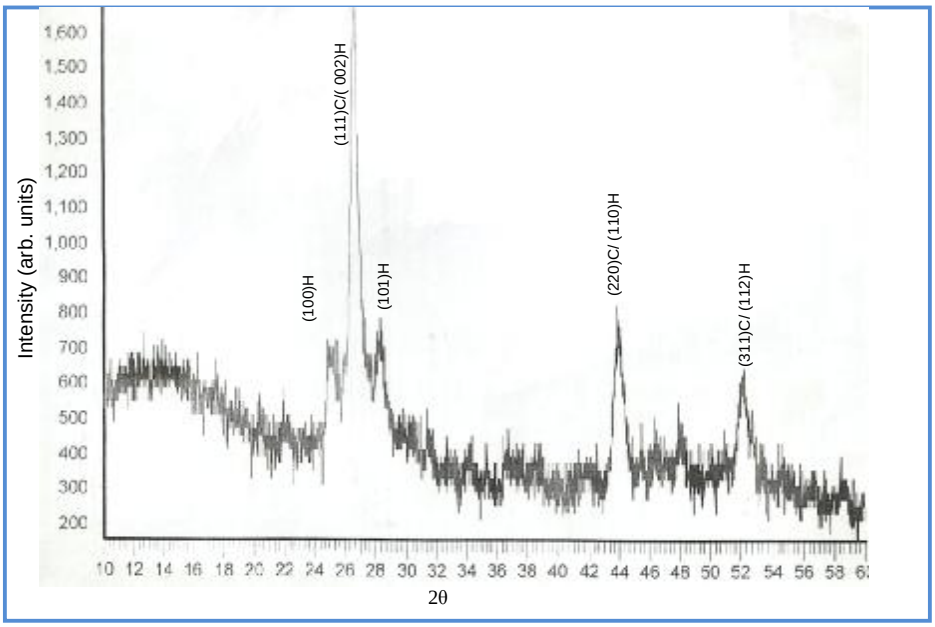

Figure (1): X-ray diffraction pattern of CdS nanoparticles.

Table(1): Result of X-ray diffraction pattern.

$2\theta^0$	(*hkl*)	Cubic(C)	Hexagonal(H)
25	(100)	-----	H
26.5	(111)C/(002)H	C	H
28.3	(101)	-----	H
44	(220)C/(110)H	C	H
52	(311)C/(112)H	C	H

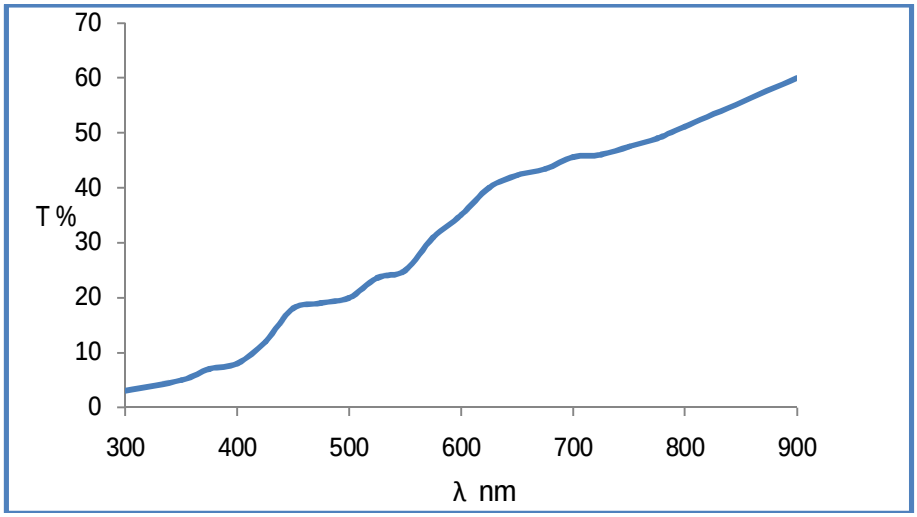

Figure (2): Optical transmission spectra of CdS nanoparticles.

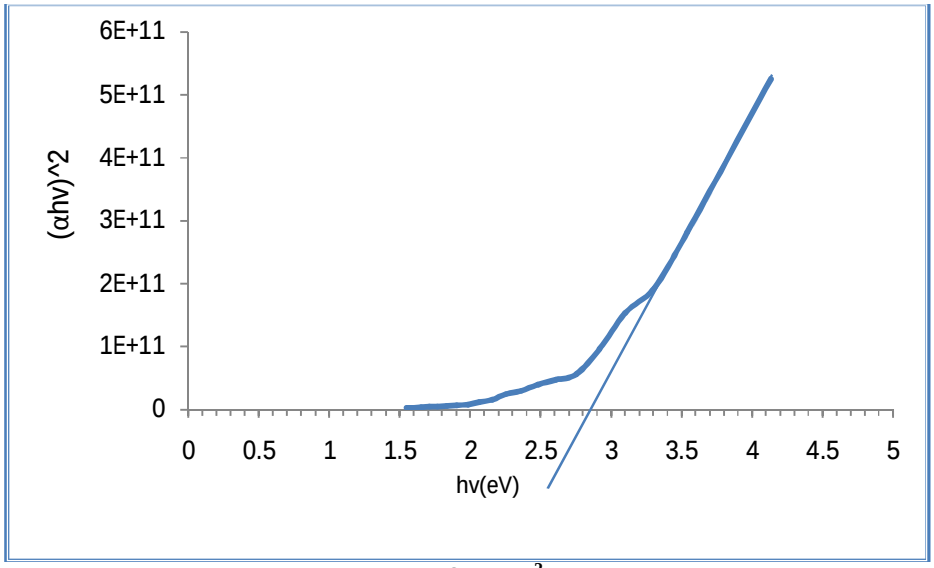

Figure (3): Variation of $(\alpha hv)^2$ vs. photon energy of CdS nanoparticles.

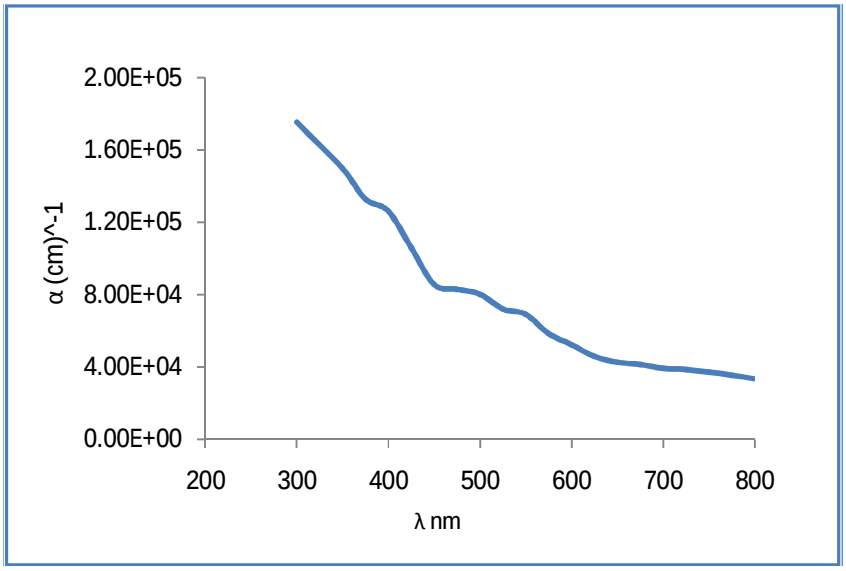

Figure. (4): Absorption coefficient vs. wavelength of CdS nanoparticles.

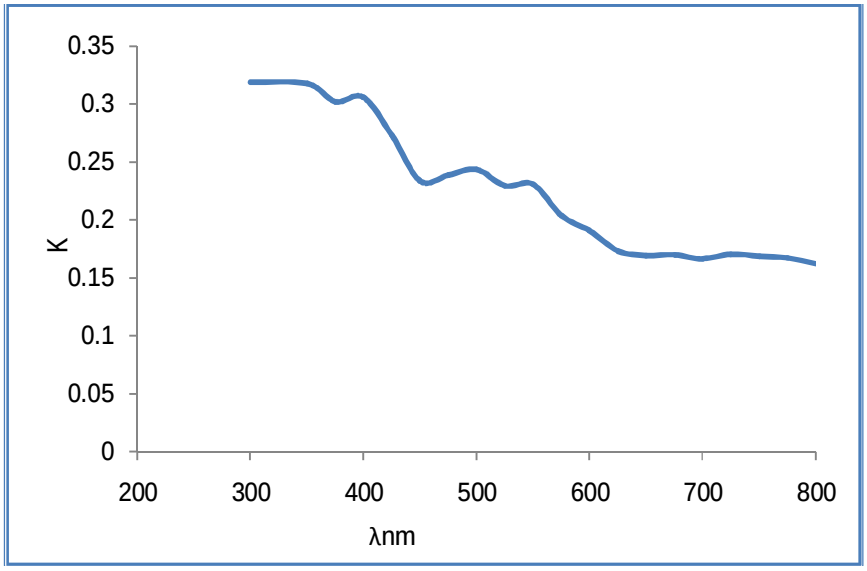

Figure (5): Extinction coefficient vs. wavelength of CdS nanoparticles.

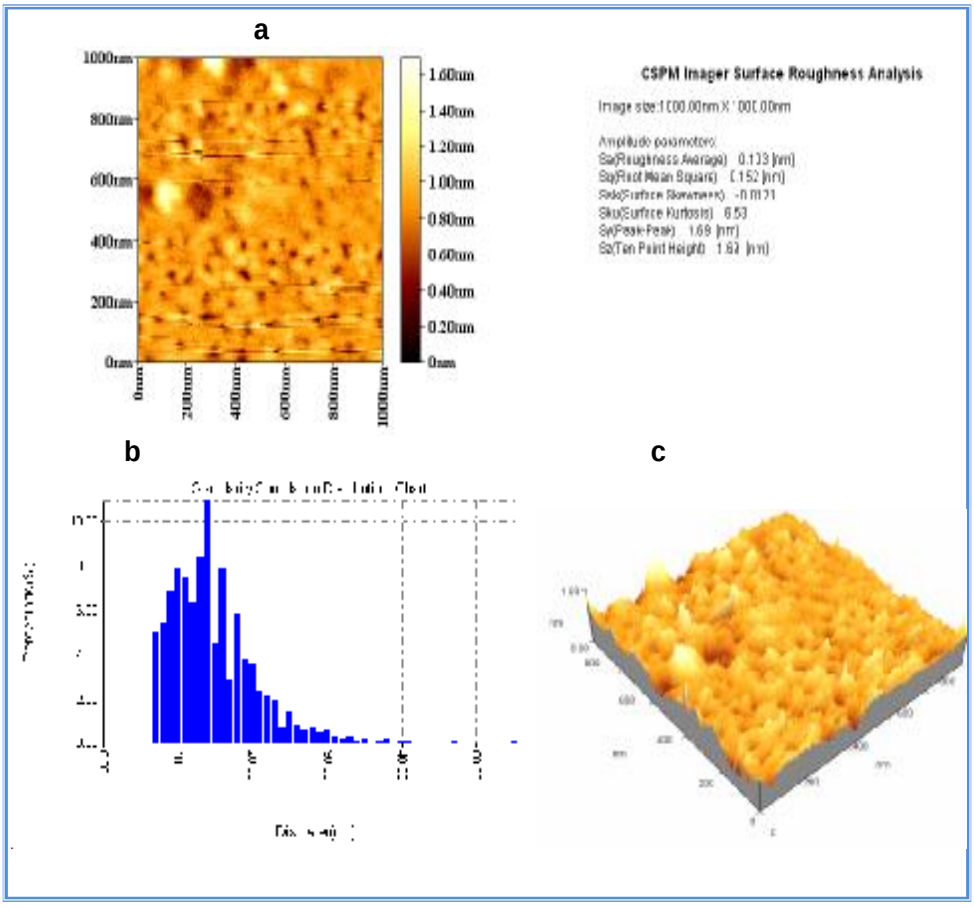

Figure (6): AFM image of CdS nanoparticles;
a) two dimensional image. b) Histogram
b) of crystal size distribution. c) three dimensional image.