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Effect of the Concentration of Copper on the Properties of Copper Sulfide Nanostructure

Zainab J. Shanan* ***Mirvat D. Majed*** ***Huda M.J. Ali***

Department of Physics, College of science for Women, University of Baghdad, Baghdad, Iraq
*Corresponding authors: zainabjassim73@yahoo.com *, mirvat.dawood@yahoo.com, hudajafarali@yahoo.com
*ORCID ID: https://orcid.org/0000-0002-5166-5200 *, https://orcid.org/0000-0002-6083-5734 , https://orcid.org/0000-0003-3261-4472

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Abstract:

Nanoparticles of copper sulfide have been prepared by simple reaction between using copper nitrate with different concentrations ratio 0.1, 0.3, and 0.5 mM, thiourea by a simple chemical route. The prepared Nano powders have been deposited onto glass substrates by casting method at 60°C. The structure of the product Nano- films has been studied by x-ray diffraction, where the patterns showed that all the samples have a hexagonal structure of covellite copper sulfide with the average crystalline sizes 14.07- 16.51 nm. The morphology has been examined by atomic force microscopy, and field emission scan electron microscopy. The AFM images showed particles with almost spherical and rod shapes with average diameter sizes of 49.11- 90.64 nm. From the UV-Vis absorption studies, it has been noted that the increased absorption edge for all thin films leads to decreases in the energy gap of 3.5 to 3.0 eV for 1mM and 5mM respectively.

Key words: Atomic Force Microscopy, Chemical method, CuS, Nanostructures, optical properties.

Introduction:

Because of its small size, the nanostructure has attracted a significant concern for its unique properties that cannot be obtained from the bulk structure. The transition metal sulfides nanostructure such as PbS, HgS, CdS, and CuS shows remarkable chemical and physical characterizations in comparison with their bulks [1]. Copper sulfide, as a member of the chalcogenide Nano crystallized semiconductor, is an important element with multifunctional utilization in industry through the solar cells [2], optical filters, sensors, photo catalysts, and lithium ion batteries [3], and other devices are inexpensive due to the high absorption coefficient ($10^4 cm^{-1}$) and small band gap (1.2 eV). NPs CuS show interesting physical and chemical properties according to their size and shape. Optical band gap energy of the CuS NPs varies from 1.2 to 2.5 eV depending on the stoichiometry. Copper sulfide NPs with different crystalline phases (such as chalcocite (Cu_2S), djurleite ($Cu_{1.9}S$), digenite ($Cu_{1.8}S$), anilite ($Cu_{1.75}S$), and covellite (CuS)) from the copper-rich (Cu_2S) side to the copper-deficient side (CuS_2) have been reported extensively [4].

Nanostructure copper sulfide shows interesting structural and optical properties depending upon various growth conditions such as molar concentration, temperature, capping agents, surfactants, precursor solution composition etc. In order to synthesize copper sulfide nanostructure different methods have been adopted such as hydrothermal route [5, 6], chemical bath deposition [1], microwave irradiation [7], green method [8], mechanochemical synthesis [9], a single step sonochemical method [10], one-step solid-state reaction [11], Spray pyrolysis deposition [12, 13], sol- gel method [14], and chemical precipitation [15, 4] and etc. Among these preparatory methods above, chemical precipitation technology is a simple, effective, and relatively low-cost method that uses the lowest possible number of chemicals, including those water-soluble minerals, and is also considered one of the most used methods for preparing nanomaterial [16].

In this research, the effect of concentration was investigated for Cu on properties of CuS nanostructures deposition by casting process. The optical, structural, and morphological properties of the prepared Nano films with different

concentrations were investigated using XRD, AFM, FE- SEM, and UV–Vis spectrophotometer.

Materials and Methods:

All chemicals and reagents were used as received without further purifications. Copper nitrate (Cu $(NO_3)_2.2H_2O$) (99.98%, from Sigma - Aldrich), thiourea (SC $(NH_2)_2$ (99%, from New Delhi - India), and polyvinyl alcohol PVA (99%, from Sigma - Aldrich) were used as raw materials for preparation CuS NPs.

Preparation of CuO Nanoparticles

In a typical synthesis, CuS nanoparticles were prepared by reacting copper nitrate solution with different concentrations 0.1, 0.3, and 0.5 mM and thiourea in the presence of polyvinyl alcohol PVA as capping and stabilizing agents. The resulting solution was greenish in color. The synthesized powders were separated from the solution with a centrifugation at 4000 rpm per minute, and washed three times with distilled water. Finally; the products were dried at 80 ^{o}C for 1hr.

Deposition of Thin film

The prepared nanomaterial was precipitated on glass substrates by casting method, at temperature 60 ^{o} C. The glass substrates were ultrasonically cleaned in acetone, rinsed in distilled water, then in ethanol, and rinsed again.

The phase and the structure characterization of the as-prepared thin films were examined by XRD using X'pert Philips diffract meter with Cu Kα radiation beam λ=1.5406 ◦A for 2 θ values between 20^{o} – 60^{o}. UV-Vis spectrophotometer SP-3000 plus, OPTIMA INC. Japan was used to measure the optical absorption measurements of samples over the range 300 nm to 1100 nm. The particle size and morphology of as- prepared thin films were studied through atomic force spectroscopy using SPM (Model AA30000), tip NSC35l//AIBS from Angstrom Advanced Inc (USA), and field emission scan electron microscopy by a MIRA3 TESCAN Mashhad (MUMS) model (Fill Emission Scanning Electron Microscope).

Results and Discussion:

Structural analysis

To characterize the crystal structure, crystalline size, and orientation factor, XRD can be used, which is powerful non-destructive means of the samples. The X- ray diffraction patterns of CuS Nano crystalline at different concentrations 0.1, 0.3 and 0.5 mM are shown in Fig. 1 a, b, c respectively.

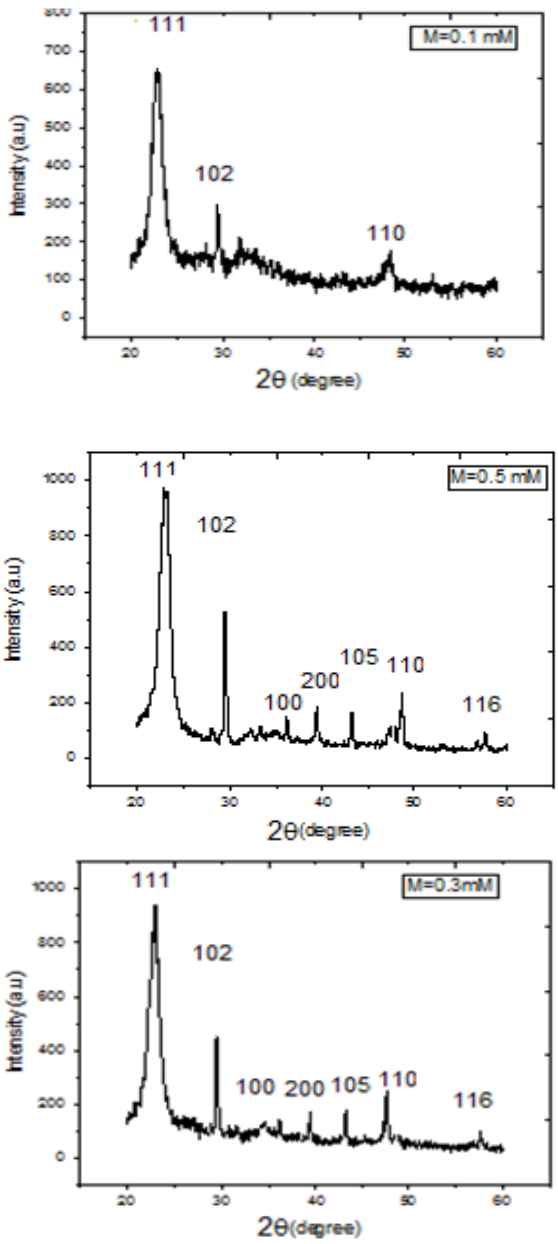


Figure. 1 XRD Pattern of CuS nano crystalline with different concentrations

From these patterns, it can be shown that the prepared thin films are of pure phase. For all the samples at different concentrations, the formation of the pure CuS was hexagonal phase. It has been affirmed by the standard peaks with the JCPDS card number 06-0464. of X-ray diffraction patterns, the diffraction peaks of the Nano crystalline were clear, indicating the formation of crystallites with Nano scale [17], these results are consistent with **M. Saranya** et al. and **S. Riyaz et al,** [4, 13].

As shown from the Figures the number of peaks increases by increasing concentration, in addition to being stronger and sharper for larger concentrations indicating that the as- prepared thin films are well crystalline but larger in size. The increasing of the crystallization and crystal size may be due to the

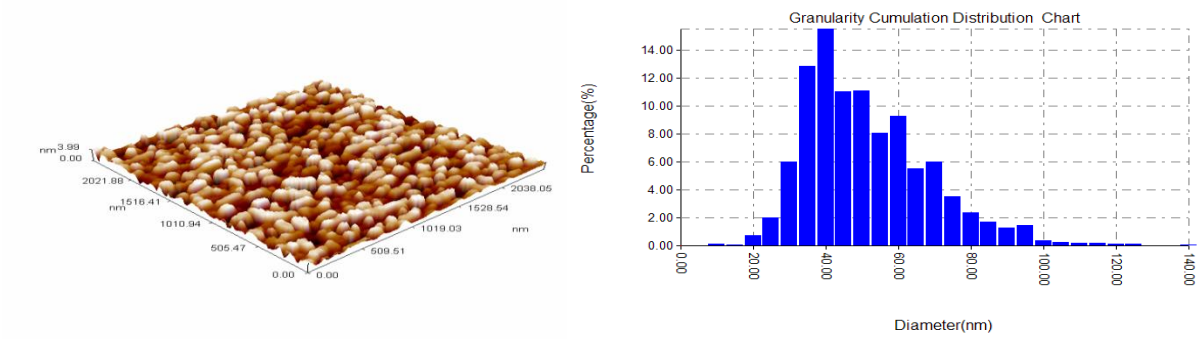
increasing of Cu concentration. The increase in the size of the crystals with increasing concentration is mainly attributable to the increase in the rate of reaction as well as on growth conditions, as the concentration increases; the crystalline nature of the film also increases. Crystallite size (D) of CuS Nano crystalline is founded using Scherrer equation ($D = 0.9\ \lambda/\beta \cos\theta$). The result values of D illustrate that the size lies within the Nano scales range as shown in Table 1.

Table 1. Illustrates the results of XRD measurements

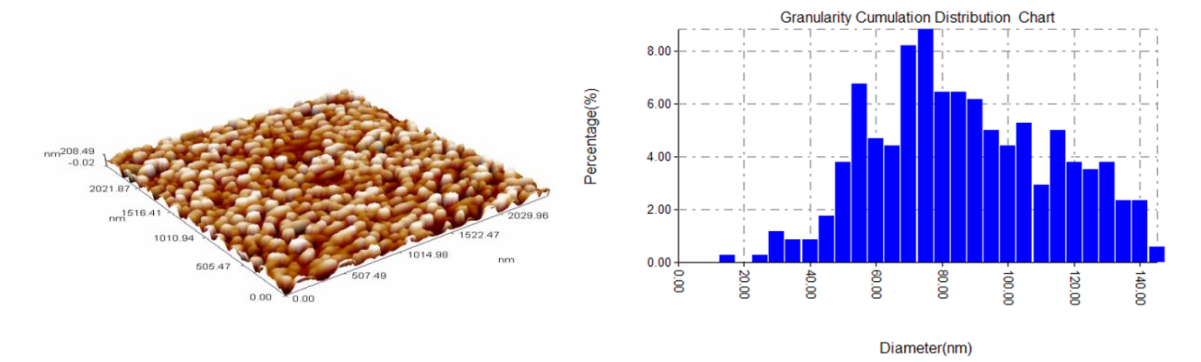
Concentration (mM)	2 θ (deg)	θ (deg)	D (nm)	D ave. (nm)	(hkl)
	22.90	0.760	10.74		100
0.1	29.5	0.516	15.92	14.07	102
	48.35	0.560	15.57		110
	22.95	0.672	12.08		100
0.3	29.55	0.420	19.15	16.35	102
	48.68	0.510	17.83		110
	23.03	0.643	12.71		100
0.5	29.55	0.402	20.44	16.51	102
	47.60	0.530	16.39		110

Morphology study by Atomic Force Microscopy

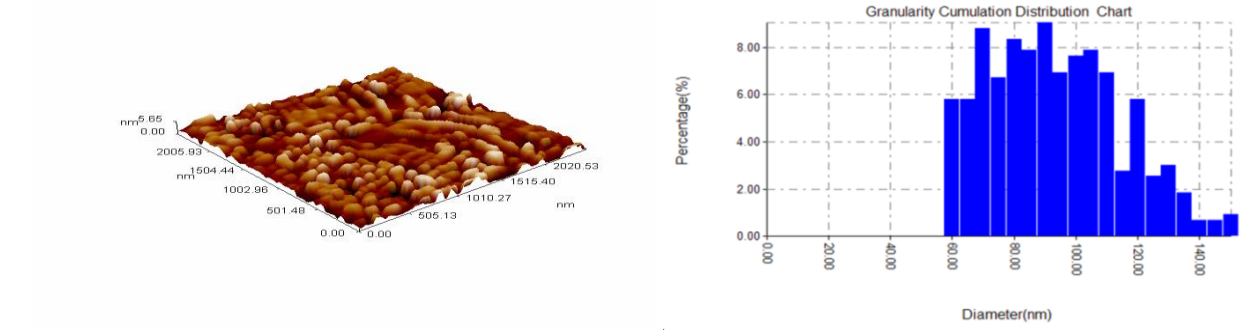
This test was utilized to examine the morphology of surface and surface roughness [18, 19]. AFM techniques give microscopic datum and topographies about the surface terrain of the nanostructures [18]. Thus, this technique progresses digital image for quantitative measurements of surface characteristics, such as three- two dimensional images, average roughness, and root mean square roughness([16]. The morphological properties for CuS Nano crystalline have been determined using Atomic Force Microscope (AFM) to observe nanostructure, also. Fig. 2 a, b, c illustrates three dimensional (3D) profile and the granular distribution of AFM micrographs for CuS films deposited at different concentrations.



(a)



(b)



(c)

Figure 2. Three dimensions and granularity distribution of CuS with different concentrations at (a-0.1 b-0.3 and c- 0.5) mM

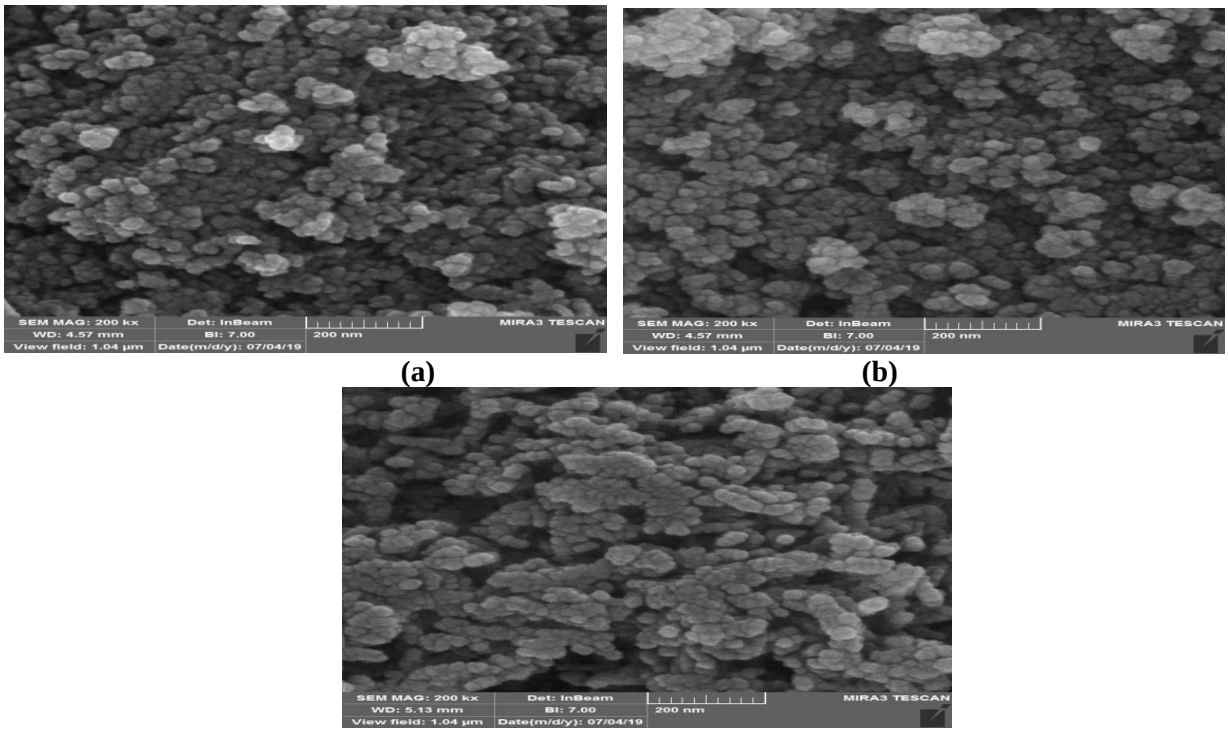
Results of AFM measurements are listed in Table 2; From these results it is noted that the mean diameter value increases with increasing concentration as well as surface roughness, root mean square, and peak to peak. These results are consistent with another work, that of M.A. Sangamesha et al. [1]. Another observation is that the grain shape was mostly spherical.

Table 2. Illustrate parameters of AFM measurements for CuS nanostructures

Concentration (mM)	Avg. Diameter (nm)	Roughness Ave. (nm)	Root Mean Square RMS (nm)	Peak – peak (nm)
0.1	49.11	0.906	1.07	3.99
0.3	84.30	0.953	1.16	5.65
0.5	90.64	46.7	54.8	118

Topography study by Fe-Sem

Figure 3 shows FE- SEM images of the CuS nanostructure synthesized at various concentrations. From the images it can be remarked seen that the surface of the particles appears almost in spherical shape with the presence of agglomeration in concentration 0.5 mM, this leads to an increase in particle size.



(a) **(b)**

(c)

Figure 3. FE-SEM images of CuS Nano crystalline at different concentration (a-0.1 b-0.3 and c- 0.5) mM

Optical Characterization of Nanostructure

Absorption spectra and transmission spectra of as- prepared thin films at different concentrations 0.1, 0.3, and 0.5 mM are shown in Figs.4, 5 respectively. The optical properties were investigated by UV-Vis spectrophotometer showing that the films have high transmission in the visible region and low absorption for all samples. This structure with notable optical properties makes it a very promising optical nanomaterial in optoelectronic devices as a window layer.

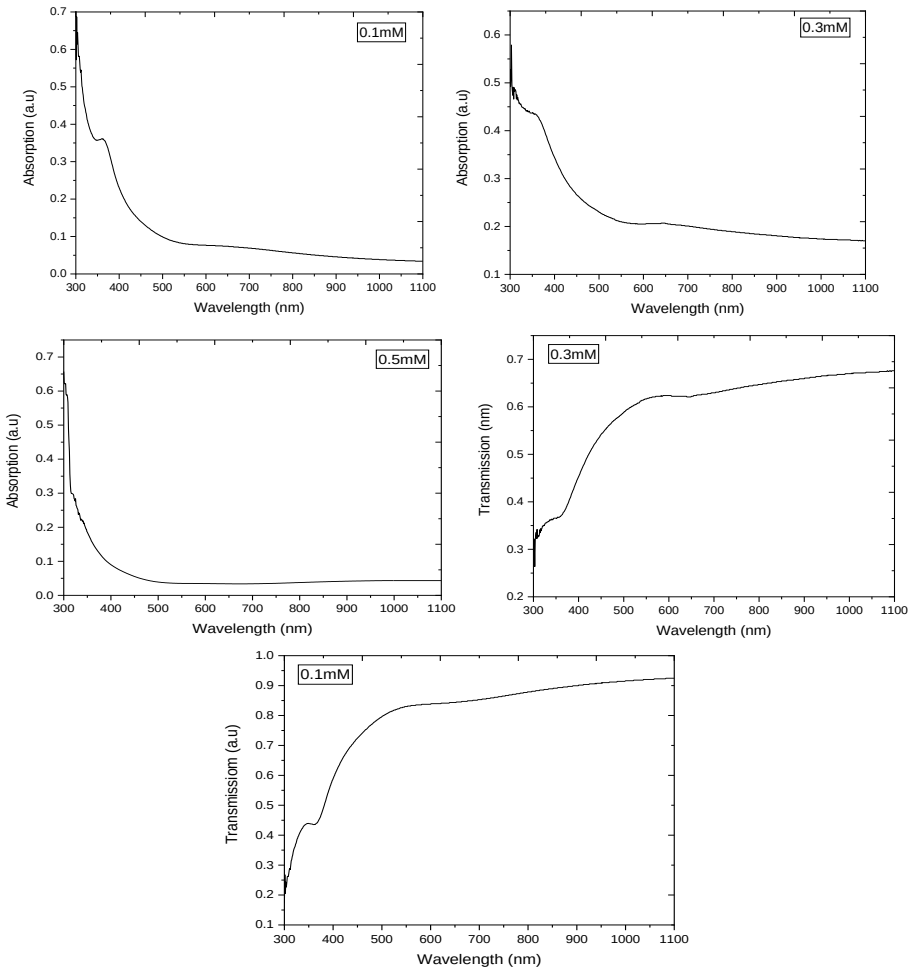


Figure 4. Absorption spectra of copper sulfide Nano films at different concentration

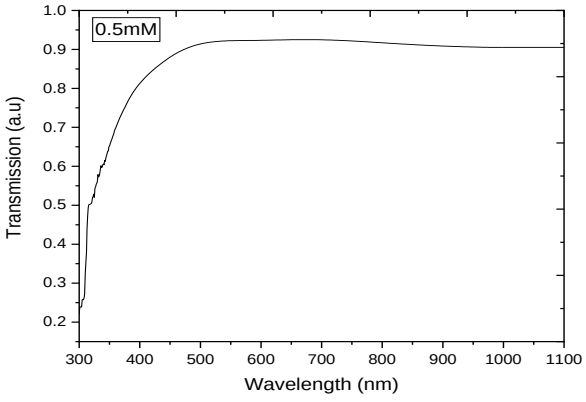


Figure 5. Transmission spectra of copper sulfide Nano films at different concentration

Figure 6 illustrates that CuS films have direct band gap which was calculated from Tauc's relation

$$\alpha h\nu = B(h\nu - Eg)^{1/2}$$

Where (hν) is the energy of the photon, (Eg) is the energy gap, and (B) is constant involving the properties of the bands. The absorption coefficient α was determined from the equation:

$$\alpha = 2.303\ A / t \qquad 2$$

where the thickness of films were 209 nm ,200 nm, and 250 nm for concentrations 0.1, 0.3, and 0.5 mM respectively. It can be noted from Fig. 6 that the band gap of (CuS) nanostructure was direct for all samples. The values of energy gap were calculated from the intersection of the straight- line portion of the $(\alpha h\nu)^2$ against the (hν). From the linear part it was noticed that the type of transition in these films has a direct nature.

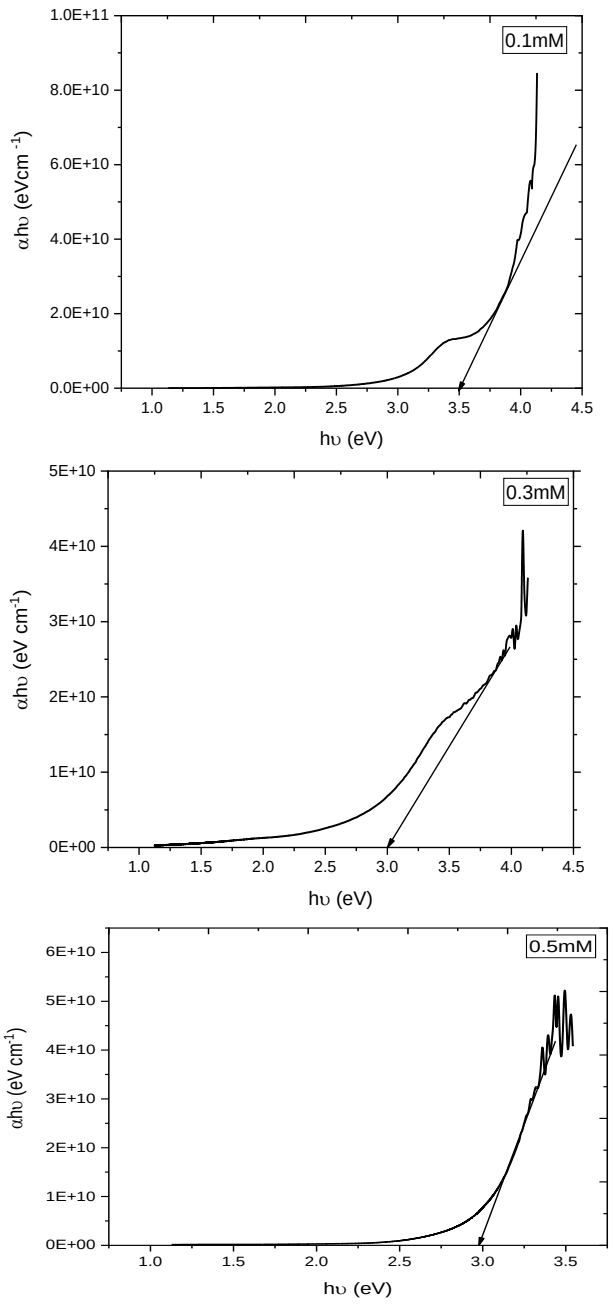


Figure 6. Energy gaps of CuS nanostructures at different concentrations

The determined energy-gap values of the samples are (3.5, 3, and 2.9) eV for (0.1, 0.3, and 0.5) mM respectively. The values of optical energy-gap for prepared nanostructures are higher compared with the bulk value of CuS (1.2 eV) due to the quantum confinement. The spectra of absorption display that the absorption peaks of exciton for the Nano crystal are blue-shifted in comparison to the bulk band gap and clearly demonstrate a strong quantum size effect [19]. Also, it has been observed that the energy gap of the films deceases when the concentration increase, this is attribute to the increase of crystalline size of the films. The results of the energy gaps are in agreement with a previous report by **M.A. Sangamesha et.al** [1].

Figure 7 illustrates the refractive index (n) with wavelength for different concentrations while Fig. 8 relates the extinction coefficient (k). The refractive index of materials is an important factor for the design of the device. The calculation of the refractive index is of great importance for applications in integrated optics.

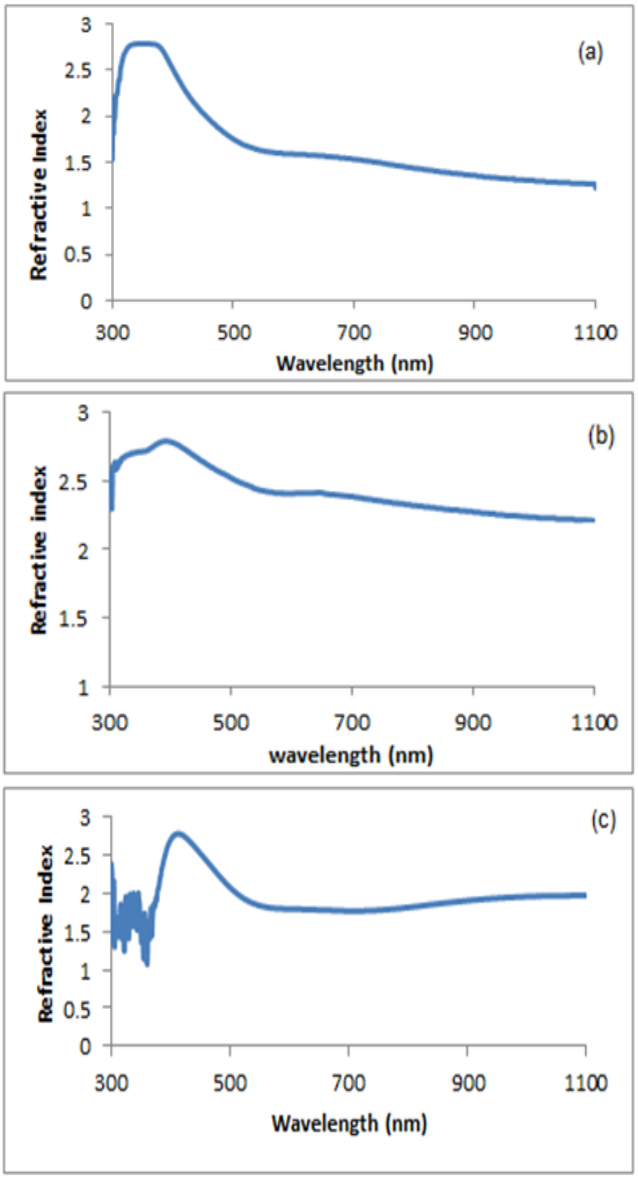


Figure 7. Shows refractive index for CuS nanostructures with different concentration a- 0.1mM, b- 0.3mM, and c-0.5mM

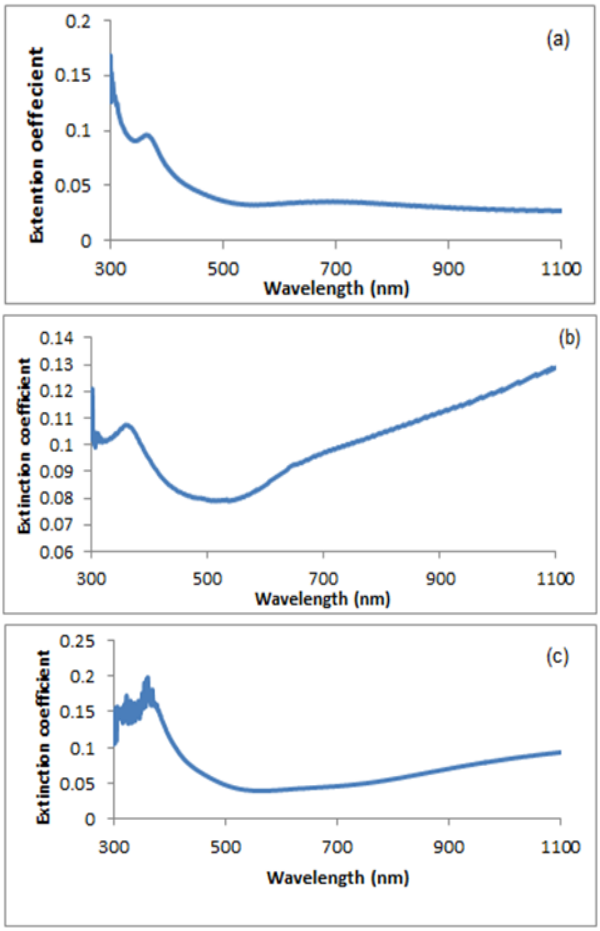


Figure 8. Shows extinction coefficient for CuS nanostructures with different concentration a-0.1mM, b-0.3mM, and c-0.5mM

The refractive index (n) can be calculated by equation

$$n = [(4R/(R-1)^2 - K^2]^{1/2} - [(R+1)/(R-1)] \quad 3$$

While the extinction coefficient (k) can be measurement by

$$k = \alpha \lambda/4\pi \quad 4$$

The values of thickness, energy gap, refractive index and extinction coefficient for the films are a tablet in Table 3.

Table 3. Shows the parameters of optical measurements for CuS nanostructures

Concentrations (mM)	Thickness (nm)	Energy Gap (eV)	Refractive Index at (550 nm)	Extinction Coefficient at (550 nm)
0.1	209	3.5	1.62	0.032
0.3	220	3	2.42	0.075
0.5	250	2.9	1.84	0.039

Conclusions:

CuS nanostructures has been synthesized by employing chemical precipitation method at different concentrations, and then deposited on glass substrate using casting method. XRD patterns show that the structural nature of the CuS thin films is hexagonal phase for the all as-deposited. The average grain size is estimated by XRD, and AFM, where that it is concluded that the size increases with increasing concentration. The shape of grains is mostly spherical that's noted from AFM, and FE-SEM images. All the films show high transmission (~ >80%) and low absorbance in the UV-VIS region. The energy gaps values decrease with increasing concentrations. The optical characterizations for as- prepared CuS nanostructures indicate that the films are useful for optoelectronic devices such as photovoltaic cell as a window layer. These nanostructures can be used as a transparent dielectric material due to their high transparency in the visible region.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Authors' contributions statement:

ZJ Shanan prepared all samples and analyzed all parameters and contributed to writing, revision and proofreading the research as well as the costs and publishing process.

MD Majed participated in sample tests, writing, revision and proofreading the research, as well as the costs and publishing process.

HMJ Ali participated in sample tests, writing, revision and proofreading the research, as well as the costs and publishing process.

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تأثير تركيز النحاس على خصائص كبريتيد النحاس النانوي لاستخدامه في تطبيقات الخلايا الشمسية

زينب جاسم شنان مرفت داود مجيد هدى محمد جعفر غفوري

قسم الفيزياء، كلية العلوم للبنات، جامعه بغداد، بغداد، العراق.

الخلاصة:

تم تحضير كبريتيد النحاس النانوي (CuS NPs) بتفاعل بسيط بين نترات النحاس بتركيزات مختلفة (0.1 و 0.3 و 0.5) ملي مول والثايوريا والماء كمذيب بأستخدام الطريقة الكيميائية. تم ترسيب المساحيق النانوية المحضرة على ارضية زجاجية بتقنية الصب وبدرجة حرارة 60 درجة مئوية. تم توصيف الأغشية النانوية الناتجة بواسطة حيود الأشعة السينية (XRD) ، مجهر القوة الذرية (AFM) ، ومجهر الالكتروني الماسح (SEM)،وأطياف الأشعة فوق البنفسجية – المرئية. أظهرت أنماط XRD أن جميع العينات كانت عبارة عن تركيب سداسي لكبريتيد النحاس وبمتوسط أحجام بلورية 14.07 - 16.51 نانومتر. بينت صور AFM اغلب الجسيمات كانت كروية الشكل وبعضها اسطوانية تقريبًا وبمعدل حجم قطر 49.11-90.64 نانومتر. من دراسة امتصاص الأشعة فوق البنفسجية ، لوحظ أن حافة الامتصاص تزداد لجميع الأغشية الرقيقة المرسبة تبعا لزيادة التركيز، مما يؤدي إلى نقصان في فجوة النطاق من 3.5 إلى 3.0 الكترون فولت للتراكيز(0.1 و 0.5) ملي مول على التوالي.

الكلمات المفتاحية: مجهر القوة الذرية، الطريقة الكيميائي، أوكسيد النحاس، الهياكل النانوية، والخصائص البصرية .