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Green synthesis of CdS:Sn NPs by Starch as a Covering Agent and Studying its Physical Properties

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Abstract:

The aim of this research is to employ starch as a stabilizing and reducing agent in the production of CdS nanoparticles with less environmental risk, easy scaling, stability, economical feasibility, and suitability for large-scale production. Nanoparticles of CdS have been successfully produced by employing starch as a reducing agent in a simple green synthesis technique and then doped with Sn in certain proportions (1%, 2%, 3%, 4%, and 5%).According to the XRD data, the samples were crystallized in a hexagonal pattern, because the average crystal size of pure CdS is 5.6nm and fluctuates in response to the changes in doping concentration 1, 2, 3, 4, 5 %wt Sn, to become 4.8, 3.9, 11.5, 13.1, 9.3 nm respectively. An increase in crystalline size has been noticed in the doped CdS than in the pure CdS. The particle size is within the range of 24-103 nm, according to SEM data from pure CdS and of the doped with Sn particles. The band gap's energy values, according to UV-Vis reflection spectroscopy were 3.06,2.61 ,2.63, 2.63, 2.66,2.69 eV for pure and doped with Sn 1%, 2%, 3%, 4%, 5% respectively. The grain size and roughness rate of pure CdS materials and doped with Sn are shown in AFM results 2.16,2.39,10.07,11.33, 12.47,18.56 nm and average diameter is 30.15, 11.71, 66.06, 48.27,82.011, 80.35 nm for pure and doped with tin 1%, 2%, 3%, 4%, 5% respectively.

Keywords: doped with Sn, Green syntheses from starch, Sn Doped CdS Nanoparticles, SEM, UV and particle size analyzer.

Introduction:

In recent years, semiconductor nanocrystals have attracted much attention in both fundamental research and technical applications owing to their unique size-dependent optical, and electronic properties [1,2] The integration of biochemistry with nanotechnology leads to an interdisciplinary platform that enhances the probability of controlling adverse effects of toxicity pervaded in nanomaterial's and the environment [3]. Various semiconductor photocatalysts show promising performance in photocatalysis. Due to their unique photocatalytic characteristics and photocatalytic properties, CdS NPs are one of the most promising photocatalysts. CdS NPs have a 2.42 eV energy gap, which is ideal for visible-light-driven photocatalysis. Large surface area, high crystallinity, short surface diffusion mass, and exciton stability are all advantages of CdS NPs in light-driven visible photocatalysis. Cd nanoparticles have been extensively explored during the past two decades, mainly due to their quantum size effects and photocatalytic properties4.Among the working gap semiconductors, in photocatalytic and bacterial studies, CdS is one of the most extensively utilized semiconductors. Nanotechnology is the study and application of particles ranging in size from one to one hundred nanometers (nanoparticles). It's one of the most rapidly growing branches of materials science in recent years, with applications in nearly every aspect of everyday life. A variety of nanoparticles have been synthesized and used for several purposes but semiconducting nanoparticles are of vital importance [5,6]. In the past few years, semiconductor materials in nanocrystalline shapes and methods for fabricating those NPs have gained great interest from researchers because of their incomparable characteristic spectroscopic and optical properties [7], and their applications in

environmental manipulation. Semiconductor nanoparticles can be used to sense and disable hazardous environmental gases and can be used to treat polluted water [8,9]. Semiconducting CdS nanoparticles are very sensitive to visible-ray detection since they are photoconductive samples in most optoelectronic devices [10] in addition to increasing.the.efficiency, of solar cells\and their\use in various\biological uses [11]. They can be used to diagnose and treat cancer due to their improved fluorescence and optical properties. Nanoparticles\can be synthesized\using many\physical and/chemical methods, such as\hydrothermal methods and thermal dissolved\methods [12,13]. However, these processes have several disadvantages, such as the use of hazardous chemicals and solvents, and they are also costly. The increasing demand for nanoparticles needs the development of ecologically friendly, low-cost, and non-toxic synthesis techniques, which may be accomplished through biological or green synthesis, which uses microorganisms, plants, and biopolymers. A large number of preparatory\techniques/have already been reported for\the\synthesis of various\metallic and non-metallic nanoparticles\using microorganisms [14,15] and different plants [16,17].The prepared material was well characterized using XRD, transmission electron microscopy, and UV-visible spectroscopy techniques. These nanoparticles exhibited a wide range of energy gaps due to quantum confinement .

In this paper, CdS:Sn nanoparticles were synthesized using starch, which in turn acts as a reducing agent as well as a covering agent. It is an alternative, safe,non-polluting method and better than traditional chemical and physical methods. These tin nanoparticles were treated with varying ratios with respect to the molarity of CdS and the importance of use in wide applications such as gas sensing, Data storage, solar cell, and also uses as antibacterial and medical applications.

Materials and Methods:

Materials:

$C_6H_{10}O_5$ (starch Supplier local in Iraq), deionized distilled water, Cd $(NO3)_2.4H_2O$ Supplier Company Qualikems, Na_2S (Thomas Baker), NaOH. $SnCl4.5H_2O$ (Thomas Baker).

Preparation of pure CdS Nanoparticle and doped with Sn:

Starch was purchased from the local market. To prepare the starch solution, 0.2 g of starch was dissolved in 400 ml of deionized distilled water and placed on a magnetic stirrer at room temperature. Then a $Cd(NO)_2.4H_2O$ solution with 0.1 molarity was prepared in deionized distilled water. Also, Na2S solution with 0.1 molarity was prepared in deionized distilled water. Then drops of NaOH solution were added and the pH was measured until it reached 8-9 . Then 2.4 ml of a solution of sodium sulfide was added to the previous substances by distillation, a yellow-orange color was obtained. The material is placed on the magnetic stirrer for 5 hours, the color will change to light yellow. Then, the solution is placed in a filtration centrifuge and washed thoroughly with a sufficient amount of deionized water and ethanol, and the material is left to dry completely. Here, pure powder nanoscale cadmium sulfide is obtained. In the same way, the doping was prepared with tin and in proportions 1, 2, 3, 4, and 5 % molar cadmium sulfide. $SnCl_4.5H_2O$ is added to the solution 1 hour after sodium sulfide distillation, then the materials are kept for 4 hours on the magnetic stirrer, and then filtered and washed with a centrifuge. Then the material was left to dry completely. CdS: Sn nanoparticles were obtained and the process was repeated with each ratio of tin mentioned above.

Characterization:

A Siemens D500 system was used to record the X-ray diffraction((XRD)) pattern of pure CdS and doped with Sn particles using; CuK, = 0.154 nm. Scanning electron\microscopy (SEM) ZEISS\Sigma VP model with a magnification of 50.00KX\Oxford Instruments UK was used to investigate particle shape and size. UV diffusion was used to examine the optical characteristics. UV-VIS (Shimadzu) was used to perform reflectance spectroscopy in the wavelength range of 300 nm to 800 nm. The AFM revealed the shape of CdS NPs in the DME Denmark model, and the cumulative distribution plot revealed the average grain size.

Results and Discussion:

XRD:

XRD was used to examine the crystalline structures of pure Cds and CdS: Sn nanoparticles placed on glass surfaces, Fig. 1 shows X-ray diffraction (XRD) patterns of pure CdS and doped with Sn at various concentrations. By comparing the data, all of the diffraction peaks were recognized as hexagonal, and the findings were consistent with JCPDS card file no. 96-900-8863. The standard data is from (100), (002), (101), (102) and the highest peak is (101). For CdS, the peaks are identical, this leads to the conclusion that doped CdS may be classified into two types: substitution and interstitial. In this case, some ions are replaced by Cd + with a Sn + ion based on radius Cd,Sn((0.9,0.73,))Å[18,19]. The nanoparticles' average grain size at half maximum breadth, the entire width

(FWHM) width Half of the wave height are calculated, then two vertical lines on the x-axis 2θ were projected from the beginning and end of the wave's mid- width, then (θ2-θ1), grain size, and 2 Θ of pure nanoparticles were calculated. Scherrer's Eq.1[20] was used to compute CdS and CdS doped with Sn

$d = \kappa\lambda/\beta\cos\theta$ 1

d: is the mean/crystalline (size, k:0.89 is the\constant, and λ=1.5418Å is the incident beam wavelength. β. The full width at half maximum is Cuk, and θ the Bragg diffraction angle is (in degrees). When the doping was increased, the crystal size grew larger. as a result of which increased (FWHM) (β) according to Scherrer Eq.1[20]

The results indicate that the six-phase nanocrystalline CdS was prepared using starch as a covering agent. And there was a slight decrease in the size of the nano-particles after doping with 1 and 2% wt of Sn and then the grain size are increasing again when doping with 3%wt of Sn. This can be seen in Fig.1 and Table. 1, that the grain size vertical to the substrate is growing while the crystal size parallel to the surface is shrinking. The former correlates to the (002) crystalline orientation, whereas the latter corresponds to the (001) crystalline orientation consistent with Naranthatta et al [21].

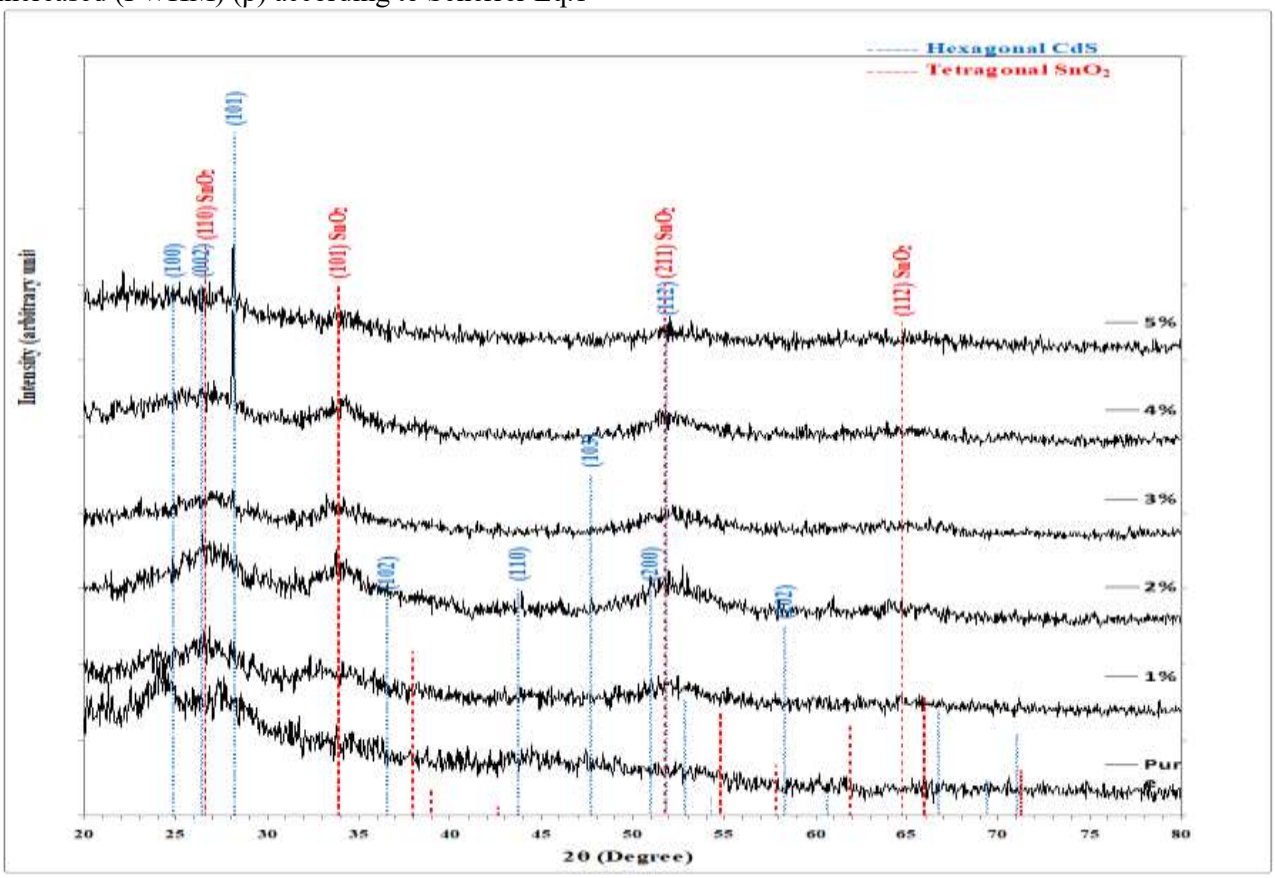

Figure 1. XRD spectrum of the CdS pure and doped with concentrations 1, 2, 3, 4, and f:5 wt. % Sn nanoparticles.

Table 1. Crystal Size of the CdS pure nanoparticles and doped with concentrations 1, 2, 3, 4, 5 %wt of Sn.

Sample	Crystallite size (D in nm)
CdS	5.675
CdS:Sn1%	4.825
CdS:Sn 2%	3.966
CdS:Sn 3%	11.54
CdS:Sn 4%	13.14
CdS:Sn 5%	16.58

SEM Measurement:

SEM images of groups of equally dispersed nanoparticles are shown in Fig.2. The majority of particles have a spherical shape. Nanoparticles are shown in the SEM data. The surface grain size is larger than the free area, which indicates that the crystal formation is of good quality and that the nanoparticles of the pure sample of CdS range between (24.5-76.06) nm and the size of the doped samples with the ratios 1, 2, 3, 4, and 5 %wt of Sn are between ((20.2- 76.05),(22.33-74.9),(22.38-76.9),(29.03-107),(26.8-123.3)) nm respectively.

The images show that the as-prepared nanoparticles are spherical and averaged different diameters and the results are in agreement with Hakeem et.al. [22] .

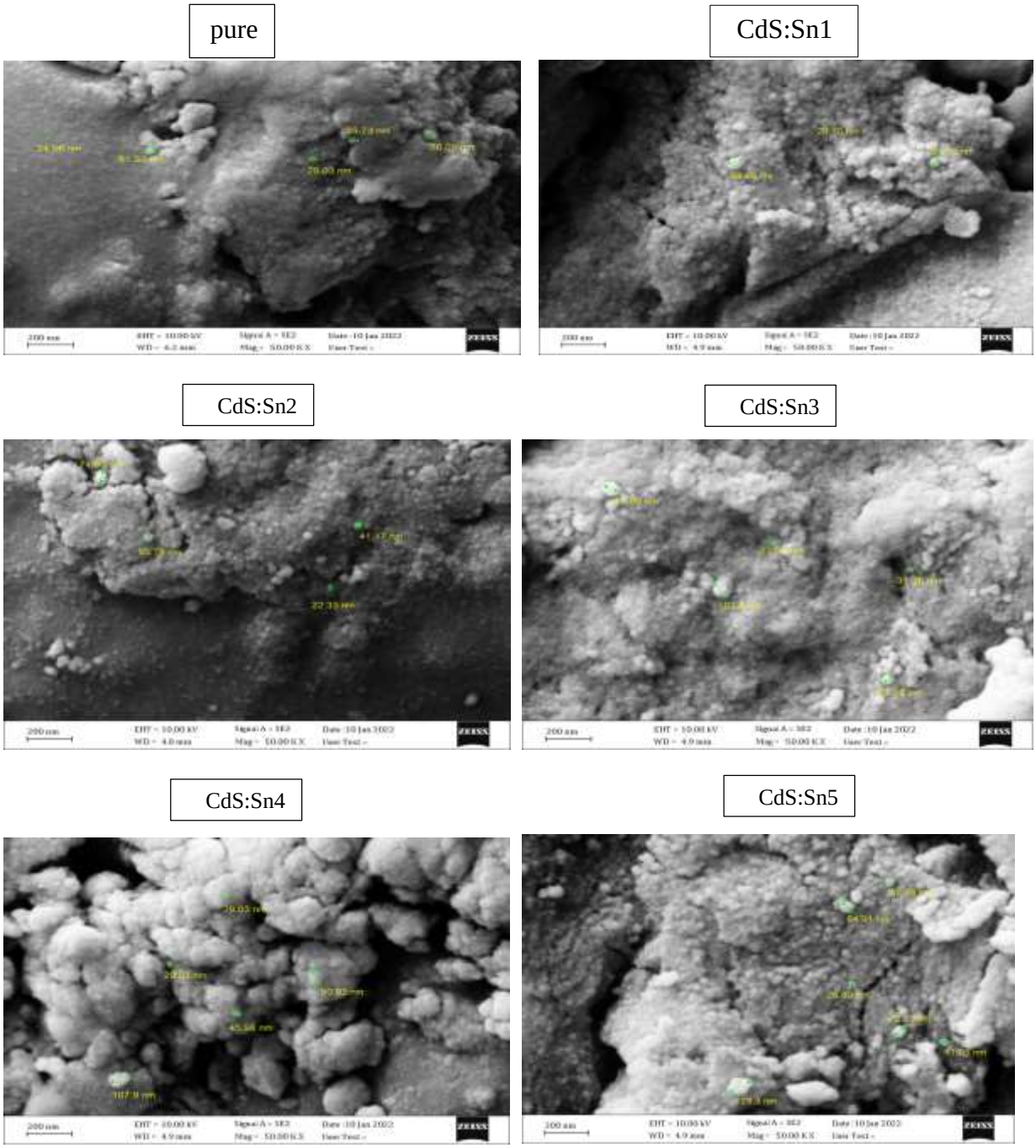

Figure 2. SEM images for CdS NPs pure and doped with 1,2,3,4,5 wt% Sn

AFM characterization:

The surface morphologies of CdS: Sn as seen in AFM pictures are shown in Fig. 3. AFM micrographs of the surface morphology of CdS: Sn nanoparticles show that the grains are evenly scattered within the scanning region, with individual vertical grains extending upwards. It is larger than the values calculated from the absorption spectrum and XRD pattern. This may be attributed to the intrinsic enlarging effect of the microscopic pinpoint to the measured nanoparticles, leading to overestimating dimensions with the AFM [22]. The larger particles from the AFM image>can be ascribed to the aggregation>of the smaller particles [23].

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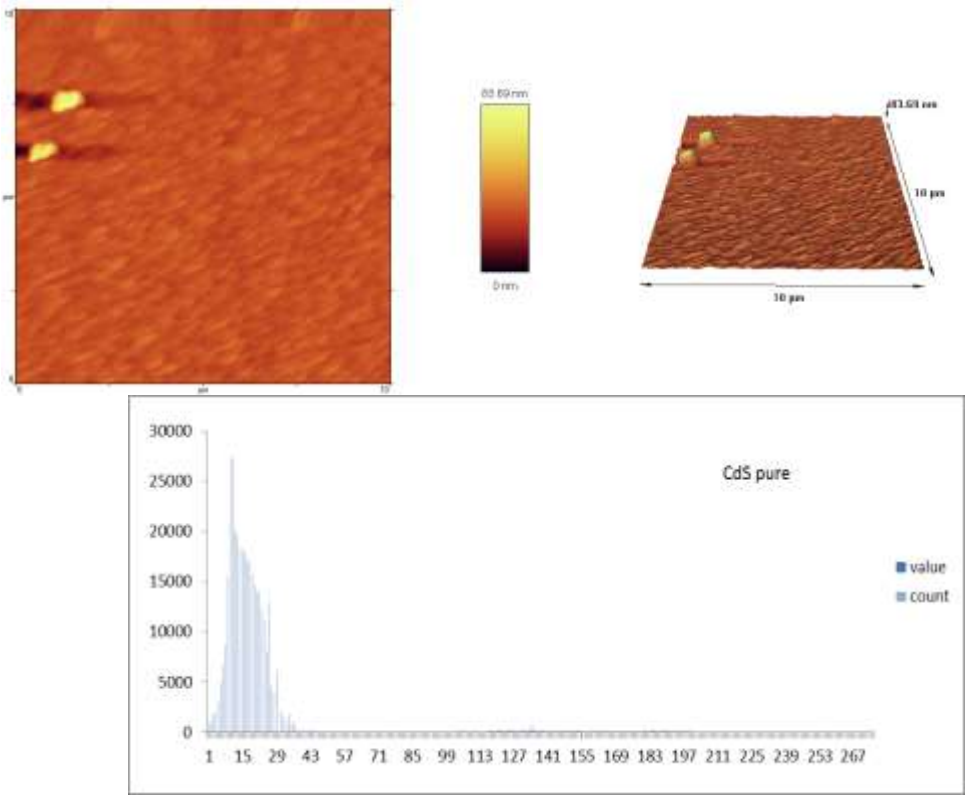

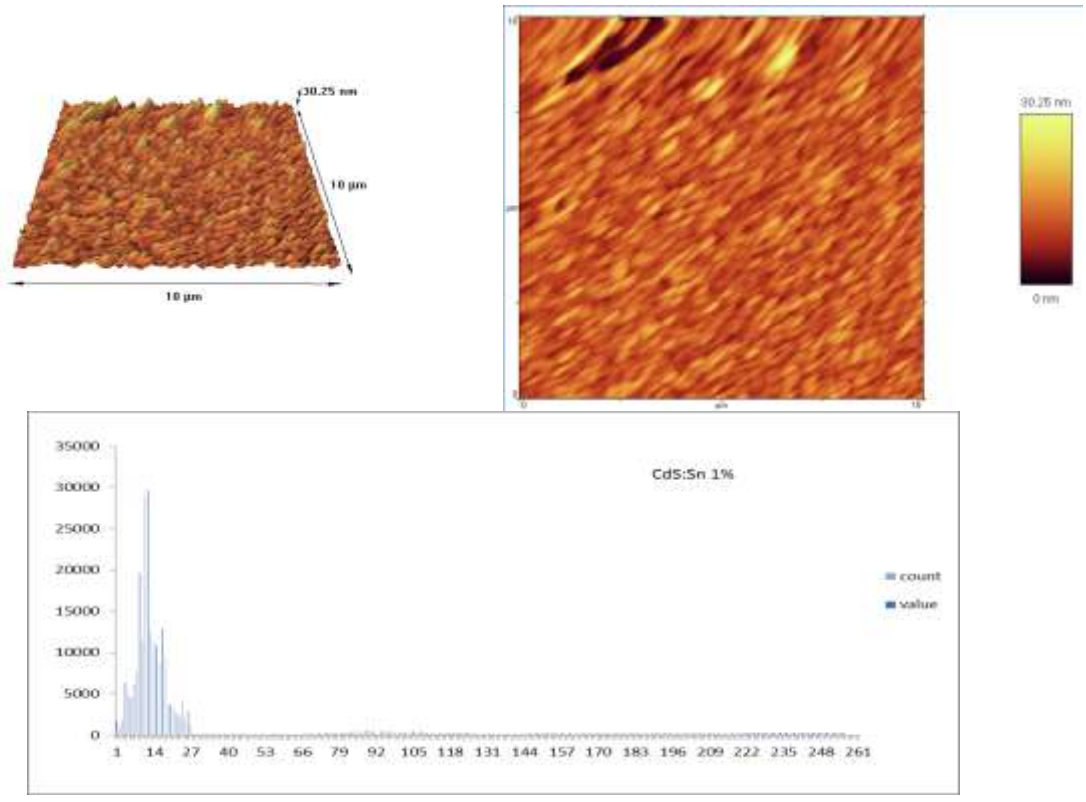

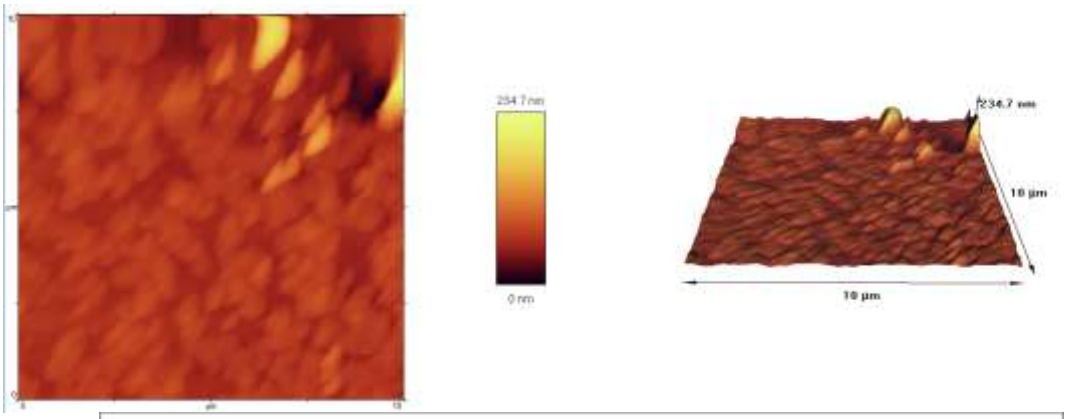
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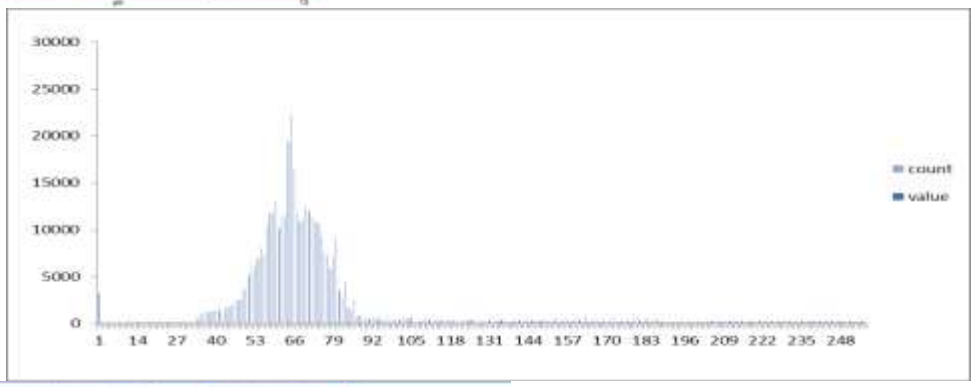
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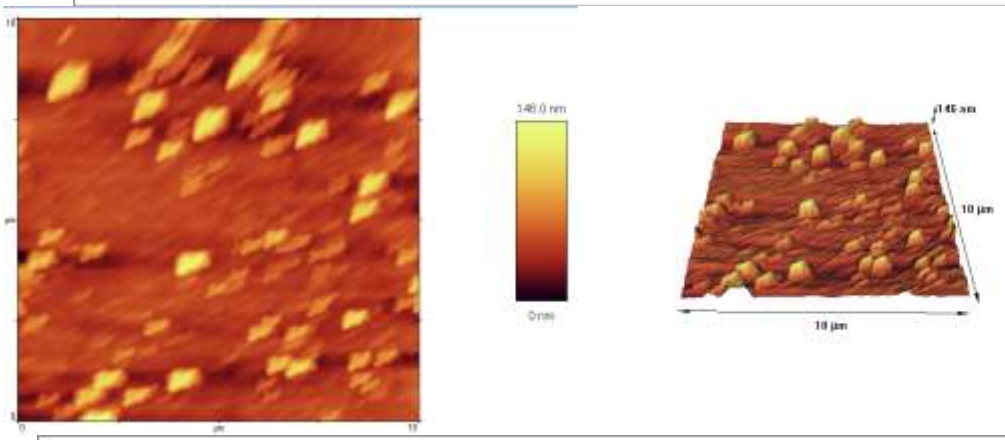
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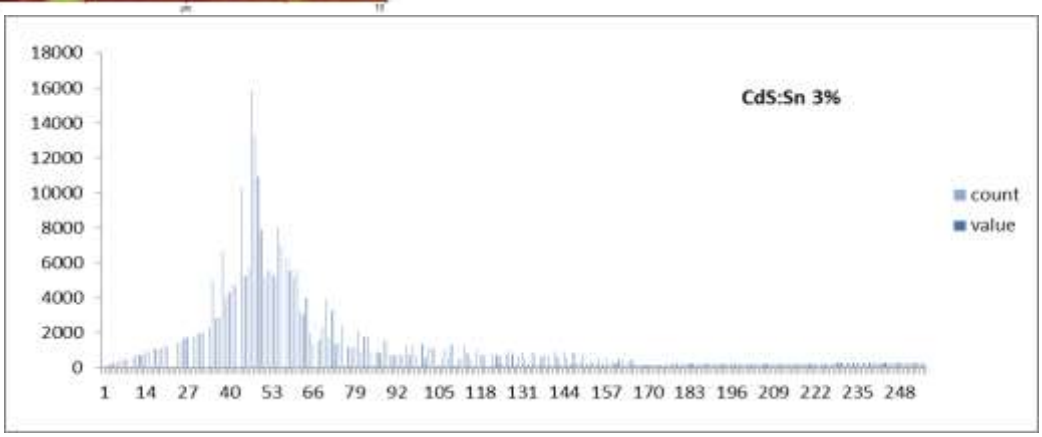
CdS:Sn 3%
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16000
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12000
10000
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2000
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1 14 27 40 53 66 79 92 105 118 131 144 157 170 183 196 209 222 235 248
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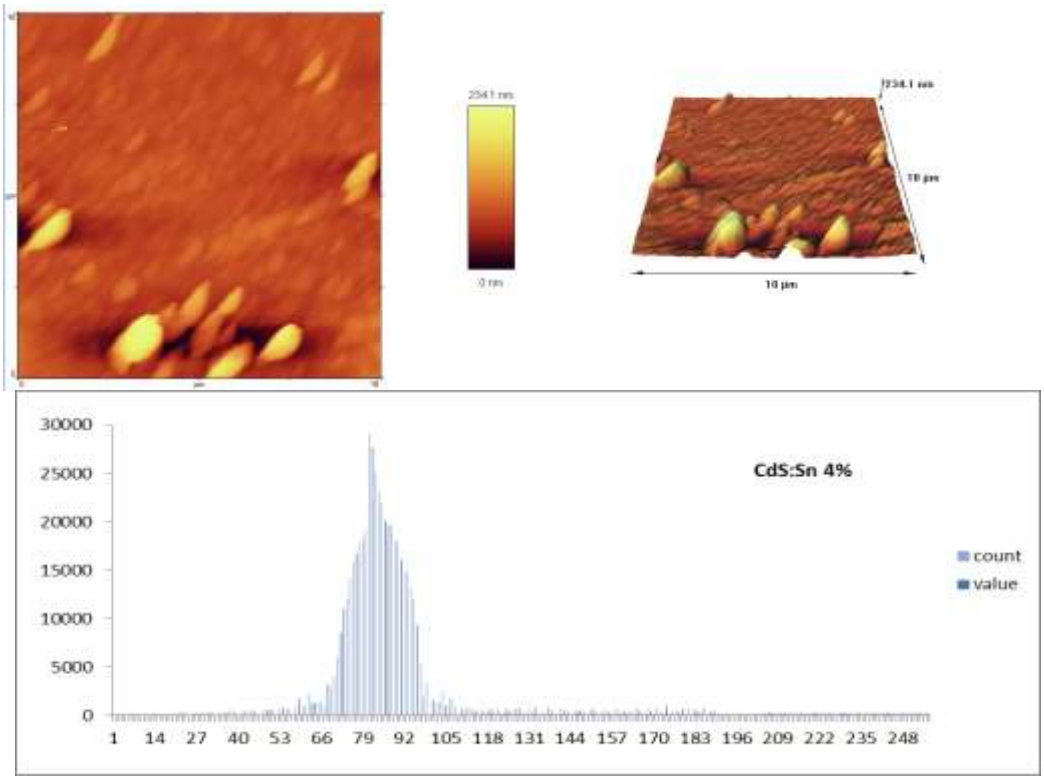

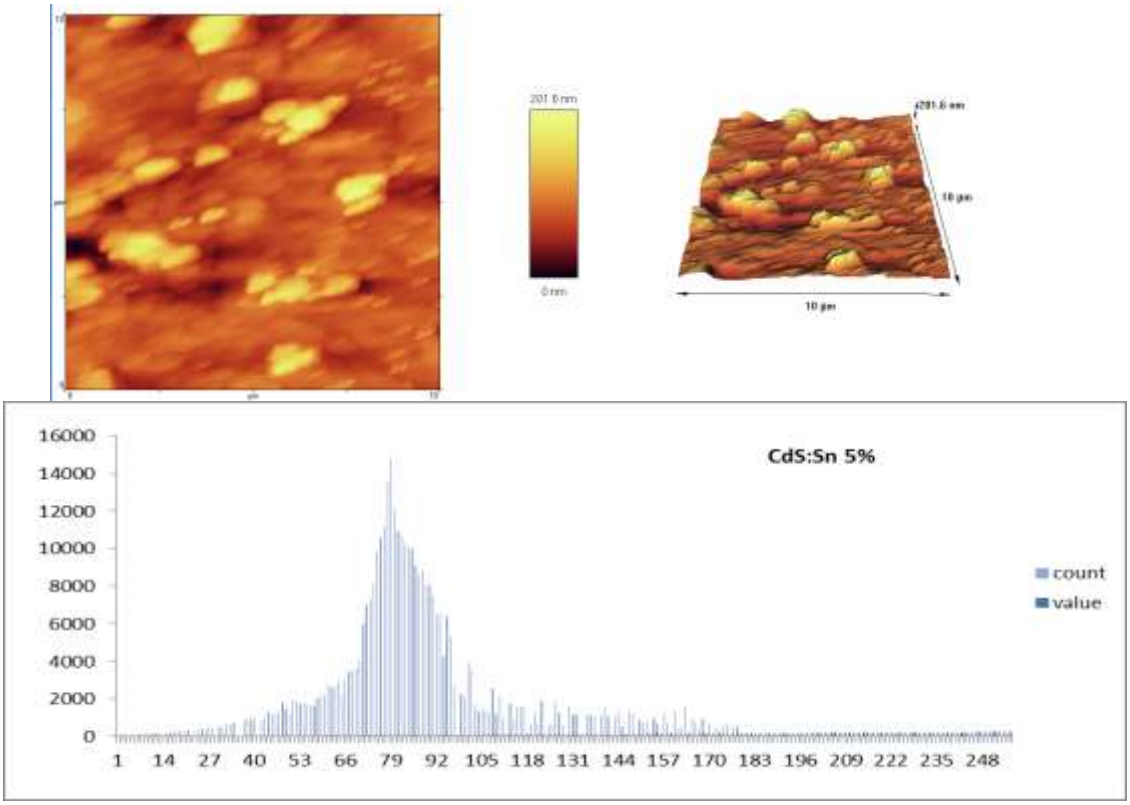

Figure 3. AFM images describing the surface morphology for CdS the pure and CdS nanoparticles doped with 1, 2, 3, 4, and 5 wt. % Sn.

Table 2. Shows the average size and roughness of pure CdS nanoparticals and those doped with 1, 2, 3, 4, and 5 wt. % Sn.

Elements	Average particle (nm)	Roughness (nm)
CdS	30.15	3.95
CdS:Sn 1%	11.71	3.127
CdS:Sn 2%	66.06	16.977
CdS:Sn 3%	48.27	17.07
CdS:Sn 4%	82.011	23.12
CdS:Sn 5%	80.35	26.7

Optical Properties Absorption: Average particle (nm)

To find out how tin doping affects the optical properties of CdS nanoparticles at different concentrations, UV-visible spectroscopy was performed. Fig. 4 shows the variation of the absorption as a function of wavelength within the confined spectral region between 300 nm to 800 nm for pure CdS samples and those doped with Sn ions, using the Planck equation, Eq.2.[24]

$E=1240/\lambda$ (ev) ……2

It is known that semiconducting nanoparticles have a distinct absorption edge and that shifting the material to the nanoscale leads to its deviation towards short wavelengths. The pure cadmium nanoparticles should have a wide energy gap due to the quantum confinement of the electron gap pair formed as a result of photon absorption of energy. The energy gap of bulk CdS is 2.42 eV for the wavelength 512 nm and the absorption peaks of pure and doped cadmium sulfide which were prepared in this paper as shown in the Table. 3. The slight decrease in the energy gap after doping with Sn is the result of a slight increase in the crystal grain size, this was given by the interpretation of the XRD results, where a slight redshift was observed for these peaks, indicating a decrease in the energy gap.

Table 3 . List of the optical energy gaps of pure CdS and CdS: Sn nanoparticles

Elements	The energy gap (eV)	wavelength (nm)
CdS	3.06	405
CdS:Sn 1%	2.61	475
CdS:Sn 2%	2.63	471
CdS:Sn 3%	2.63	471
CdS:Sn 4%	2.66	466
CdS:Sn 5%	2.69	460

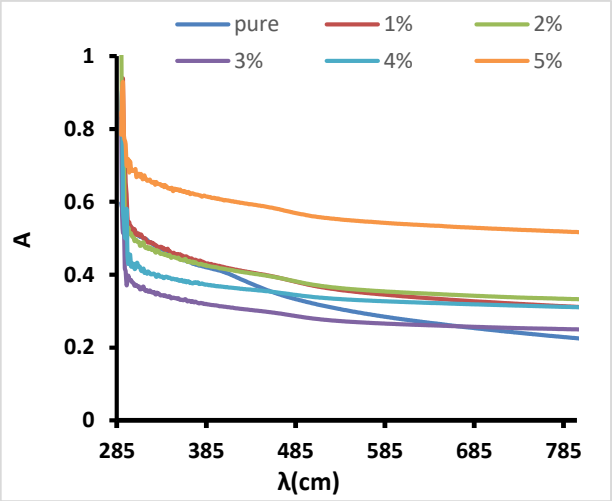

Figure 4. Uv-Vis spectrum of pure CdS and doped d with (1, 2, 3, 4, and 5) % wt. Sn nanoparticles.

Conclusions:

This study includes the synthesis of CdS nanoparticles and is performed by the green synthesis method using starch which acts as a covering agent or stabilizer for reducing the particle size of cadmium sulfide into nanoparticles. A simple, economical, and the environmentally friendly route has been developed for the synthesis of cadmium sulfide nanoparticles using starch coating agents. Crystal size is calculated by XRD data of nanoparticles using, and nanoparticle size is measured from SEM data obtained from nanoparticle size.

This method by which cadmium sulfide nanoparticles have been obtained is environment friendly for commercial production as it does not involve the use of hazardous and toxic sealing agents. Moreover, the concentration of the capping agent has a significant effect and can be seen in the crystal size, and a shift was seen in λ max.

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:

N. K. A. conceived of the presented idea and supervised the findings of this work. Z. Y. developed the theory and performed the computations and verified the analytical methods.

All authors discussed the results and contributed to the final manuscript

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التوليف الأخضر لـ CdS: Sn NPs باستخدام النشا كعامل تغطية ودراسة خصائصه الفيزيائية

زينب يعقوب **ندى خضير عباس**

قسم الفيزياء، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق

الخلاصة:

تهدف الدراسة الحالية إلى استخدام النشا كعامل استقرار واختزال لتخليق الجسيمات النانوية CdS مع مخاطر بيئية أقل ، وقابلة للتحجيم بسهولة ، ومستقرة ، ومجدية اقتصاديًا ، ومناسبة للإنتاج على نطاق واسع ، وقد تم تصنيع الجسيمات النانوية CdS بنجاح عن طريق تخليق أخضر بسيط طريقة استخدام النشا كعامل اختزال ثم المشوب مع Sn بنسب معينة (1٪ ، 2٪ ، 3٪ ، 4٪ و 5٪) أظهرت نتائج XRD أن العينات تبلورت في الشكل السداسي. نظرًا لأن متوسط حجم بلورة CdS يبلغ 5.6 نانومتر ويختلف مع تغير نسب التشويب (1٪، 2٪، 3٪، 4٪، 5٪) بالوزن (9.3،13.1،11.5،3.9،4.8) نانومتر على التوالي، لاحظ أن زيادة في الحجم البلوري في المشوب منه في النقي. وأكدت نتائج SEM من الجسيمات النقية والمشوبة أن حجم الجسيمات يقع في نطاق (24-103) نانومتر. كشفت دراسات الأشعة فوق البنفسجية-المرئية عن التحليل الطيفي للانعكاس أن طاقة فجوة النطاق تزداد مع زيادة نسب التشويب (2.61،3.06، 2.63، 2.63, 2.69،2.66) الكترون فولت مقابل (1 ٪، 2 ٪، 3 ٪، 4 ٪، 5٪) من CdSالنقي و المشوب بـ Snعلى التوالي. أظهرت نتائج AFM معدل الخشونة وحجم حبيبات العينات النقية و المشوبة بالـ Sn حيث كان معدل الخشونة لـ CdS (11.33،10.07،2.39،2.16، 18.56،12.47) نانومتر ومتوسط القطر(30.15, 11.71 ,66.06, 82.011 ,48.27, 80.35) للنقي والمشوب بالقصدير (1٪، 2٪، 3٪، 4٪، 5٪) على التوالي.

الكلمات الرئيسية: مشوب بـ Sn، التوليف الاخضر من النشأ، جسيمات CdS النانوية المشوبة بـ Sn, SEM ، UV ومحلل حجم الجسيمات.