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Fabricated of Cu Doped ZnO Nanoparticles for Solar Cell Application

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Abstract:

Copper with different concentrations doped with zinc oxide nanoparticles were prepared from a mixture of zinc acetate and copper acetate with sodium hydroxide in aqueous solution. The structure of the prepared samples was done by X-ray diffraction, atomic force microscopy (AFM) and UV-VIS absorption spectrophotometer. Debye-Scherrer formula was used to calculate the size of the prepared samples. The band gap of the nanoparticle ZnO was determined by using UV-VIS optical spectroscopy.

Keywords: Zinc oxide nanoparticles, Zinc acetate, Copper acetate, X-Ray Diffraction, Atomic Force Microscopy.

Introduction:

The studies of semiconductor nanoparticles trigger have a big attention in the last years, that is due to their optical uniqueness and electrical properties (1). Recently, the synthesis characterization and processing of nanostructure materials are emerging and rapidly growing research work (1, 2). Zinc oxide is a versatile material and well known to have a direct band gap of 3.37 eV at room temperature and has distinguishable performance in electronics, optics and photonics (3, 4, 5, 6). Among the semiconductor nanoparticles, zinc oxide is an important II-VI semiconductor, which has been researched extensively, according to its broad spectrum of potential applications such as in catalysts (7). Zinc oxide is an important multifunction material, which has received considerable attention over the past few years due to its unique applications in microelectronics and photovoltaic devices, the self-assembled growth of three-dimensional nanomaterials. It is used for various high tech applications, such as optical devices, solar cells, piezoelectric devices, surface acoustic wave (SAW) devices, and gas sensors (8). In recent years, a lot of efforts are made to dedicate the investigation of doped metal chalcogenide nanostructure materials.

This type of nanoparticles appears high improvement in the physical and chemical properties compared with the materials as in bulk, such as the energy of band gap of size-dependent were dissimilarity.

Furthermore, these nanostructures doped with ion impurities can be affected the eventualities of transitions and electronic structure (9). Nanostructure ZnO materials have received broad interest because of their outstanding performance in electronics, optics, and photonics. Since 1960s, syntheses of thin films of ZnO have been an active field due to their applications, as gas sensors, transducers, and catalysts (10). The purpose of the research is to prepare the zinc oxide nanoparticles and study the structure and optical properties, then synthesis the dopant of ZnO nanoparticles with different copper concentrations for the possibility of decrease the energy gap and thus to be used in the manufacture of solar cells.

Materials and Methods:

ZnO:Cu nanoparticles have been prepared via chemical co-precipitation method at room temperature. Zinc acetate ($C_4H_6O_4Zn \cdot 2H_2O$), copper acetate $Cu(CH_3COO)_2$, and sodium hydroxide (NaOH) were used to synthesis ZnO:Cu nanoparticles. Molarities for solutions were 0.3M, 0.001M and 1M for zinc acetate, copper acetate and sodium hydroxide respectively, which were prepared in separated flask. Cu doped ZnO with concentrations (0%, 6%, 9%, 12%, 18%, and 30%) nanoparticles have been prepared in distilled water by the chemical co-precipitation method. Copper

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acetate solution and zinc acetate were manufactured in distilled water and mixed with volumetric ratio with continuous stirring. Aqueous solution of 10% sodium hydroxide is synthesized separately with a wise drop of the mixture with strong agitation by a magnetic stirrer at room temperature. Sodium hydroxide solution was added until precipitate was obtained, and then the precipitate was washed three times using distilled water to remove impurities in the precipitate. The sediment was dried at room temperature for 24hrs. Sediment products obtained in the furnace are annealed at 100 ° C for 1 hour in air.

The crystalline structure, size of the nanoparticles and phase purity were determined by XRD technique. X-ray powder diffract meter with copper filtered monochromatic $\text{CuK}\alpha$ radiation ($\lambda=1.54 \text{ \AA}$). Samples were scanned to the desired extent for rates (20-80)°. The measurements of optical absorption that are obtained from solution were performed in ultraviolet-V spectroscopy. The

morphology and roughness of surface were investigated by atomic force microscopy (AFM).

Results and Discussion: Structural Studies

The structure of Copper doped ZnO nanoparticles was examined by X-ray diffraction of powder. The XRD patterns of nanoparticles of pure ZnO and ZnO doped with Cu are shown in Fig. 1. In Fig. 1, the peaks of X-ray have been found to be corresponded to (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes of the ZnO hexagonal phase (JCPDS 36-1451). The structure of ZnO remains almost unchanged by the incorporation of the copper but the peaks have been widened, this indicates that the prepared material is a nanoparticle. In all patterns the peaks are not detected corresponding to the impurities. The expansion of non-doped and doped samples indicates the formation of ZnO nanoparticles. Average grain size, 2θ , and FWHM for pure ZnO and ZnO:Cu are listed in Table 1.

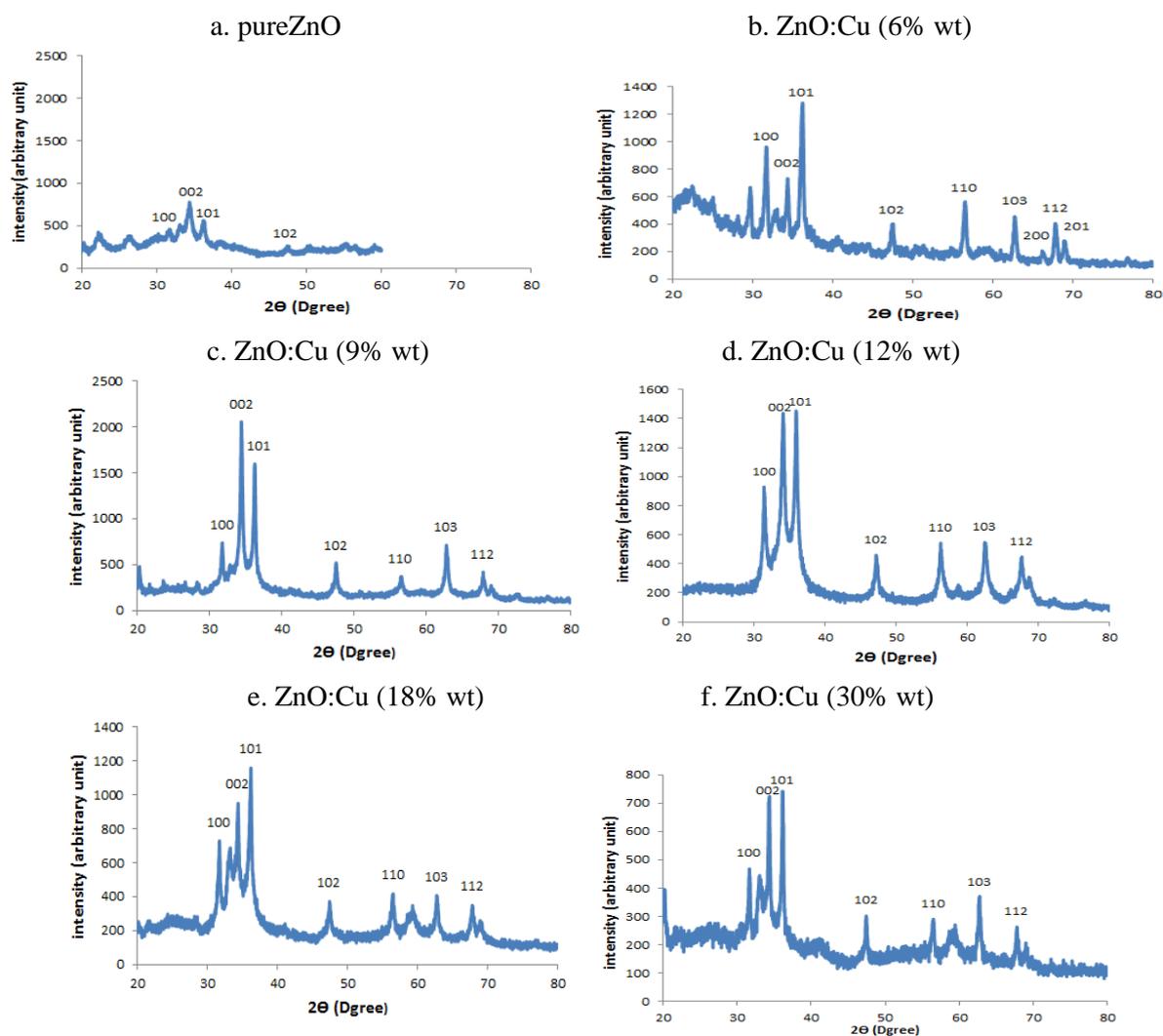


Figure 1. XRD spectrum of pure ZnO and ZnO nanoparticles doped with (a: 0, b: 6, c: 9, d: 12, e: 18, and f: 30) % wt. Cu.

Table 1. Crystallite size variation with dopant materials

| Samples | 2 θ (Deg.) | FWHM(Deg.) | G.S(nm) |
|----------|-------------------|------------|---------|
| Pure ZnO | 31.36 | 0.006 | 24.3 |
| | 34.3 | 0.008 | 18.2 |
| | 36 | 0.006 | 24.3 |
| | 46.8 | 0.003 | 51.3 |
| 6% Cu | 31.67 | 0.005 | 28.87 |
| | 34.34 | 0.003 | 49.5 |
| | 36.1 | 0.006 | 24.3 |
| | 47.3 | 0.003 | 51.3 |
| | 56.45 | 0.005 | 31.5 |
| | 62.66 | 0.003 | 33 |
| | 66 | 0.005 | 33.8 |
| | 67.7 | 0.003 | 57.75 |
| 9% Cu | 68 | 0.005 | 33.8 |
| | 31.4 | 0.005 | 28.87 |
| | 34.06 | 0.008 | 18.2 |
| | 35.9 | 0.006 | 24.31 |
| | 47.15 | 0.006 | 25.66 |
| | 56.25 | 0.008 | 19.8 |
| | 62.4 | 0.006 | 27.7 |
| 12% Cu | 67.5 | 0.005 | 33.8 |
| | 31.7 | 0.005 | 28.8 |
| | 34.4 | 0.008 | 18.2 |
| | 36.2 | 0.006 | 24.3 |
| | 47.45 | 0.003 | 51.3 |
| | 56.4 | 0.003 | 53.3 |
| | 62.7 | 0.006 | 27.17 |
| 18% Cu | 67.8 | 0.005 | 33.8 |
| | 31.7 | 0.005 | 28.8 |
| | 34.38 | 0.003 | 49.5 |
| | 36.2 | 0.006 | 24.3 |
| | 47.4 | 0.005 | 30.8 |
| | 56.4 | 0.005 | 31.5 |
| | 62.7 | 0.003 | 55.44 |
| 30% Cu | 67.7 | 0.005 | 33.8 |
| | 31.65 | 0.003 | 49.5 |
| | 34.28 | 0.005 | 29.48 |
| | 36.1 | 0.005 | 29.17 |
| | 47.37 | 0.003 | 51.3 |
| | 56.4 | 0.005 | 31.5 |
| | 62.68 | 0.006 | 27.17 |
| 67.7 | 0.005 | 33.39 | |

The average crystallite size is calculated using Scherer formula (11,12).

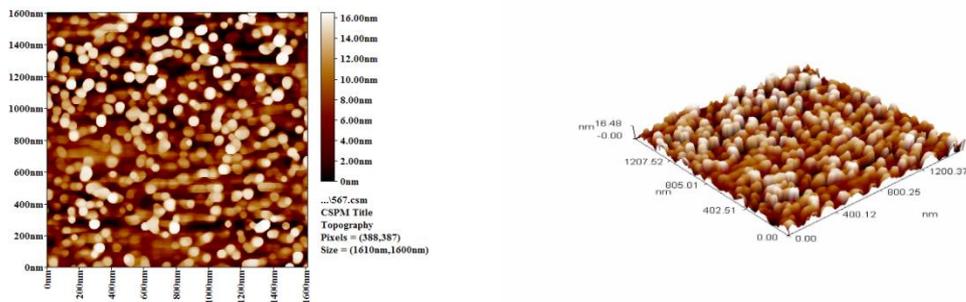
$$D = 0.9\lambda / \beta \cos\theta \quad \dots (1)$$

The quantity D is the crystallite size, θ is the angle of the diffraction peak, λ is the wavelength of the X-ray incident (1.54 \AA), β is the full width at half maximum of the XRD peak.

The average crystallite size measured of pure ZnO and doped with Copper nanoparticles displays that nanoparticles prepared in the quantum confinement system as shown in Table (1). These results are consistent with Shaveta and Labhane (11, 13).

Surface Morphology

a. pure ZnO



b. ZnO:Cu (6% wt)



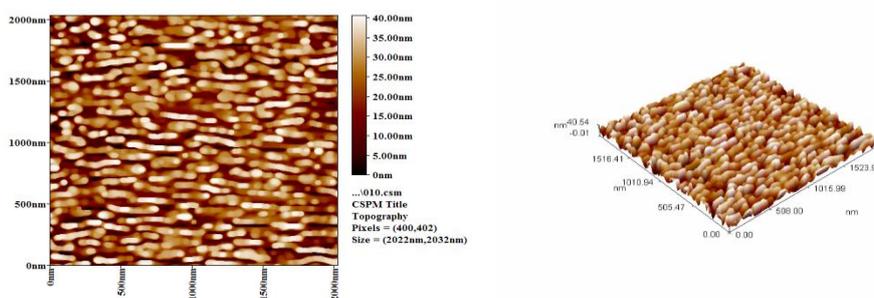
c. ZnO:Cu (9% wt)



d. ZnO:Cu (12% wt)



e. ZnO :Cu (18% wt.)



f. ZnO:Cu (30% wt)

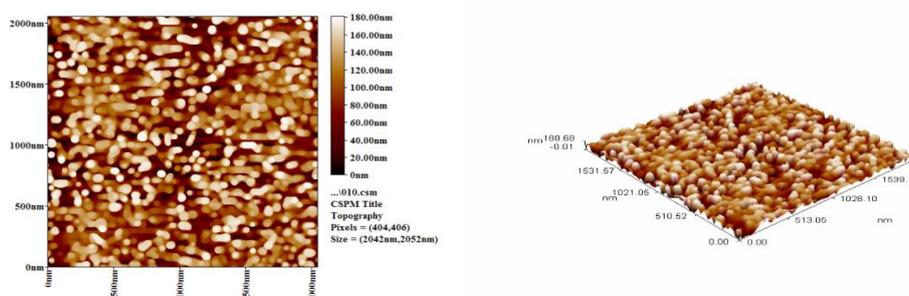


Figure2. Atomic force microscopic images of ZnO:Cu nanoparticles. Two-dimensional (2D) and three-dimensional (3D).(a) pure ZnO and ZnO Doped with Cu.

Atomic force microscopic (AFM) allows us to obtain microscopic information for topographic mapping to represent the surface relief and structure. The technique shows digital images that allow for quantitative measurements of surface characteristics, such as square root roughness, Rq, or average roughness Ra, and analysis of image from different perspectives, including 3D simulation (9). Fig. (2) shows two dimensional (2D)

and three dimensional (3D) images of pure ZnO and ZnO:Cu.

Average grain size in diameter of ZnO: Cu (0, 6, 9, 12, 18, and 30)% wt. are recorder in Table 2 .It can be observed that there is a statistical discrepancy in the values obtained, which depends on the location of the measurements that are made on the specimens (9).

Table 2. Grain size and average roughness of pure ZnO and ZnO:Cu nanoparticles.

| Sample | Grain size (nm) | Roughness (nm) | Peak to peak(nm) |
|-----------------|-----------------|----------------|------------------|
| Pure | 77.08 | 4.04 | 16.4 |
| ZnO:Cu (6% wt) | 106.26 | 4.92 | 22.3 |
| ZnO:Cu (9% wt) | 80.65 | 3.64 | 14.5 |
| ZnO:Cu (12% wt) | 85.01 | 15.8 | 70.6 |
| ZnO:Cu (18% wt) | 72.96 | 8.35 | 40.4 |
| ZnO:Cu(30% wt) | 75.12 | 36.4 | 177 |

It can be observed that the concentration of the dopant is increased, the increment and decrement were observed in grain size and roughness nanoparticles. When the grain size increased, it is noticed an increment in roughness and when the grain size decreased, the roughness decreased is shown in Table 2. Those results are in agreement with literature (14, 15).

Optical Properties

The absorption spectrum of non-doped ZnO nanoparticles and doped ZnO are displayed by Fig. (3). Fig. (3 a) shows the absorption peak at wavelength 343nm, which is due to the absorption of nanoparticles zinc oxide. The absorption edge shifted towards shorter wavelengths when ZnO doped with Cu, and the shifting increases with increment of concentration of Cu as shown in Fig. (3 b-f), that means an increment occurred in energies gap for ZnO nanoparticle.

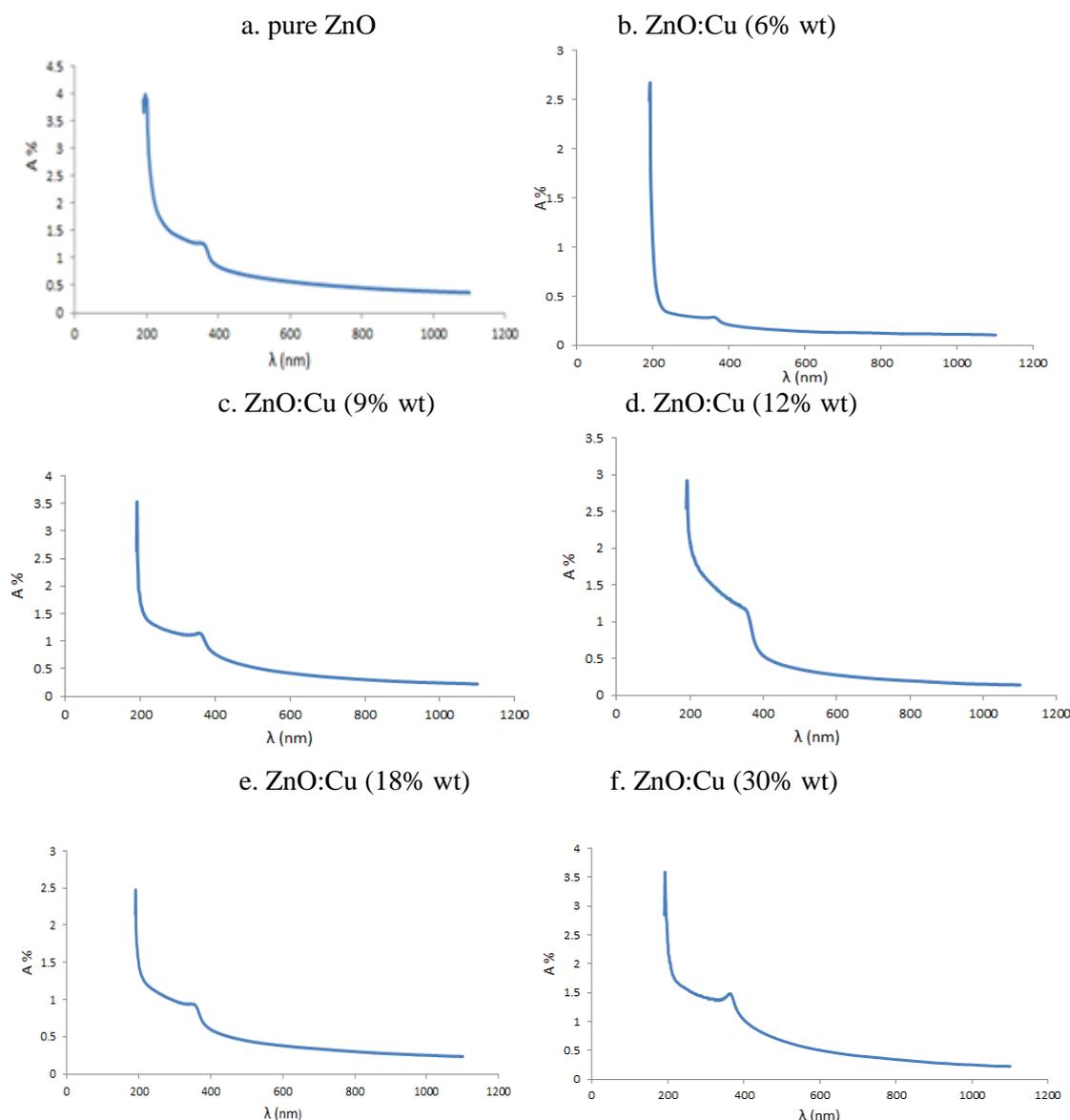


Figure 3. Absorption spectra of pure ZnO doped with Cu nanoparticles.

The energy gap of ZnO nanoparticles was measured from the absorption peak using the following relationship

$$E_{gn} = h\nu_{gn} = hc/\lambda_{gn} \dots \dots (2)$$

Where h is plank's constant, E_{gn} is the energy gap of the semi conducting nanoparticles in the optical spectra, and c is light velocity. Energy gap for pure ZnO and ZnO:Cu are listed in Table 3.

Table 3. Energy gap of un-doping ZnO and Cu doping ZnO

| Cu concentration (wt) | Energy gap (eV) |
|-----------------------|-----------------|
| 0% | 3.615 |
| 6% | 3.59 |
| 9% | 3.65 |
| 12% | 3.62 |
| 18% | 3.58 |
| 30% | 3.53 |

Table (3) shows that as the concentration of the dopant is increased by (9%) so that the energy gap increased, while at concentrations of the dopant (6, 12, 18, 30)% shows a decrement in the energy gap. This decreasing in energy gap values was explained as a result of formation of levels of copper impurities within the energy gap, and these levels are increased by increasing the deflection rates.

Conclusion:

Nanoparticles of ZnO:Cu were prepared via a simple aqueous chemical bath technique. The structural properties were examined by XRD, which show the samples prepared in hexagonal phase. The crystallized sizes were calculated via the Debye-Scherrer relation, it was about (18.2-55.4) nm. Optical properties and band gap were determined by

UV-Vis spectra. The energy gap values for pure zinc oxide and doped with copper nanoparticles were found to be decreased from 3.61 to 3.53 eV. Optical absorption measurements revealed that the absorption edge was shifted towards longer wavelengths. The morphology surface of the prepared nanoparticles was studied by Atomic force microscopy images. When doping increased, an increment and decrement were observed in grain size and roughness nanoparticles.

Conflicts of Interest: None.

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تشكيل جسيمات أكسيد الزنك النانوية المطعمه بالنحاس لتطبيقات الخلايا الشمسية

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الخلاصة:

تم تصنيع أكسيد الزنك النانوي المطعم بتركيز مختلفة من النحاس بطريقة الترسيب الكيميائي عند درجة حرارة الغرفة بواسطة التفاعل البسيط بين خلات الزنك وولات النحاس مع هيدروكسيد الصوديوم في محلول مائي. ومن ثم درست الخصائص البصرية للمادة المصنعة بواسطة طيف الأمتصاص الأشعة فوق البنفسجية والمرئية والخصائص التركيبية بواسطة حيود الأشعة السينية (XRD) ومجهر القوة الذرية (AFM). تم حساب حجم الحبيبة للمادة المحضرة بواسطة علاقة ديبي-شيرر من طيف الأشعة السينية ومن طيف الأمتصاص. وأجريت دراسة التحليل الطيفي الضوئي UV-VIS لتحديد فجوة الطاقة من أكسيد الزنك جسيمات متناهية الصغر.

الكلمات المفتاحية: أكسيد الزنك النانوي، خلات الزنك، خلات النحاس، حيود الأشعة السينية، مجهر القوة الذرية.