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Synthesis of CuO Nano structure via Sol-Gel and Precipitation Chemical Methods

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Abstract

CuO nanoparticles were synthesized in two different ways, firstly by precipitation method using copper acetate monohydrate $Cu(CO_2CH_{13})_2 \cdot H2O$, glacial acetic acid (CH3COOH) and sodium hydroxide(NaOH), and secondly by sol-gel method using copper chloride($CuCl_2$), sodium hydroxide (NaOH) and ethanol (C_2H_6O). Results of scanning electron microscopy (SEM) showed that different CuO nanostructures (spherical and Reef) can be formed using precipitation and sol- gel process, respectively, at which the particle size was found to be less than 2 µm. X-ray diffraction (XRD)manifested that the pure synthesized powder has no inclusions that may exist during preparations. XRD results showed the particles size of highest peak at 38.9°, was equal to (15.93nm). In addition, Fourier transform infrared spectroscopy (FT-IR) were used to describe the prepared CuO nanostructures absorption peak at 610 cm^{-1} which confirms that the synthesized product is a pure CuO and may be attributed to Cu_2O infrared active mode.

Keywords**:** *CuO nanostructure, precipitation method, sol- gel method.*

1. Introduction

Nanotechnology is a unique branch of science that deals with materials in a very small size between (1-100 nm) with different crystal shapes such as spherical nanoparticles, flower like, Nano rods, Nano ribbons, Nano platelets. The matchless physical and chemical attributes are result from its high surface-to-volume ratio comparing with micro or bulk-sized [1]. Authorship of high-durability nanomaterials with keeping to chemical pureness, phase selectivity, crystallinity ، and analogy in particle size with controlled state of agglomeration in a cost-effective procedure is still a challenge to material chemists [2] Various methods have been used to produce CuO. These comprise; rapid precipitation, spin coating, solid state reaction, chemical vapor deposition, sonochemical reaction, sol-gel route, chemical bath deposition, solvothermal process, electrochemical method, spray pyrolysis, thermal oxidation and hydrothermal route. [3]

The precipitation and hydrothermal routes are predominating used because they are friendly to the environment , safe and the most attractive and practical route that could be used because of its cost- performance and simple implementation is the quick precipitation method [4].

Of all the above composition procedures sol-gel process has many beneficial. Solitary sol-gel installation can yield materials at ultra-low temperatures, synthesize nearly any substance, co-synthesize two or more substances with each other, exactly observance the microstructure of the end outputs, and punctually dominance the physical ،mechanical, and chemical characterizes of the final outputs [5].

Since the chemical and physical attribute of CuO just based on its size and morphology, so numerous researchers have centered their endeavor on the found of nano construction of CuO in order to stratify them in Nano electronics, optoelectronics, biosensors etc [3]. CuO nanomaterials have the merit of a low surface potential partition than that of metals, which

influence on electron field release possession. CuO consider as a potential field emitter, an strong catalytic factor, as well as a valid gas sensing substance. It likewise shows a significant assignment in optoelectronics and solar cell. The metal elements are capable to compose a large variety of oxide compounds. These can take on a great number of constitutional geometries with an electronic structure that able to display metallic,semiconductor or insulator individuality.[6]

Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and high density of corner or edge surface sites. Particle size is expected to influence three important groups of basic properties in any material. The first one comprises the structural characteristics, namely, the lattice symmetry and cell parameters. Bulk oxides are usually robust and stable systems with well-defined crystallographic structures. However, the growing importance of surface-free energy and stress with decreasing particle size must be considered: changes in thermodynamic stability associated with size can induce modification of cell parameters and/or structural transformations , and in extreme cases the nanoparticle can disappear due to interactions with its surrounding environment and the high surface-free energy . Nanomaterials have become important owing to their small size and large surface area. They exhibit unique properties which are not seen in bulk materials [7]

In the present investigation, we have synthesized CuO nanoparticles using low cost sol-gel process and the most safe and environmentally friendly precipitation method.

2. Experimental Work

2.1. First Route: Chemical Precipitation

In order to prepare the nano copper oxide by precipitation route, it was done in two stages: the first was dissolving 1.5g of copper acetate monohydrate($Cu(CO_2CH_3)_2 \cdot H_2O$) in 300 ml of distilled water and then added three drops of glacial acetic acid in a volumetric flask at high mixing speed and 32 ^{0}C. The second stage: dissolving 8 g of sodium hydroxide in 200 ml of distilled water was added drop by drop to the prepared solution in the first stage which turns from bright blue to dark blue, and leaved for one day to turn black. Centrifuge machine is used to filter the black sludge(15min and 490rpm) and washed with water. The sample allowed to dry at room temperature then annealed at temperature 700°C using Carbolite CWF 1200 DegC, 1200 laboratory chamber furnace. The annealed sample of copper oxide nanoparticles was grinded.

2.2. Second Route: Sol- Gel method

The synthesis of nano copper oxide by sol-gel method was as fellow: 0.9 g of copper (II) chloride was dissolved in 25 ml of ethanol, 1.5 g of sodium hydroxide was dissolved in 80 ml ethanol. The prepared sodium hydroxide solution was added drop wise to copper chloride solution with constant stirring at room temperature for 30 min .Reaction occurs and colour turns from dark blue to black .Filter paper is used to filter the gel and washed with water. The sample allowed to dry at room temperature then annealed at temperature 700°C using Carbolite CWF 1200 DegC, 1200 laboratory chamber furnace. The annealed sample of copper oxide nanoparticles was grinded.

For the two routes The crystal structure of the CuO nanostructure has been determined by X-ray diffraction (Philips PW 1050 X-ray diffract meter of 1.5^{o}A from Cu-Kα, Fourier Transform Infrared Spectroscopy (SHIMADZO IRAFFINITY) and the surface morphology of CuO nanostructure were examined by Scanning Electron Microscope (SEM-VACAN).

3. Results and Discussion

3.1. X-Ray Diffraction Analysis

X-ray crystallography considered a tool used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. The crystal structure of CuO nanoparticles prepared by both methods has been showed in Fig. (1) at CuKα (λ = 1.54056 A) in the 2θ range from 20° to 80°. The crystallite sizes of the particles were calculated by using Scherrer's equation.

$$D = K\lambda / \beta\cos\theta \quad ....(1)$$

Where,

D is the crystallite size of the particles,

K is a shape factor (K=0.9 in this work),

λ is the wavelength of the incident1 X-ray (1.54056 A, CuKα),

θ is the diffraction angle and β is the fullwidth half maximum.

X-ray diffraction (XRD) pattern higher intensity peaks located at 38.9°, 35.6° and 48.9° which corresponds to the atomic planes (111), (¯111) and (¯202) respectively. These diffraction planes were well fit with Mohammed *et.al* [8] who prepare Copper(II)-oxide (Cu=O) nanostructures with different sizes and shapes and their applied in different man daily life applications. In this study the particles size of highest peak (38.9°), is (15.93nm). Table 1, shows size, diffraction angle, Full width at half maximum, d spacing and diffraction Plane of CuO sample.

Table 1,
Size, diffraction angle, Full width at half maximum, d spacing and Diffraction Plane of CuO sample.

Peak no.	Diffraction angle [degree]	FWHM [radians]	d spacing [nm]	Diffraction Plane
1	38.96	0.0093	2.3095	100
2	35.68	0.0116	2.5138	67
3	48.92	0.0085	1.8602	26

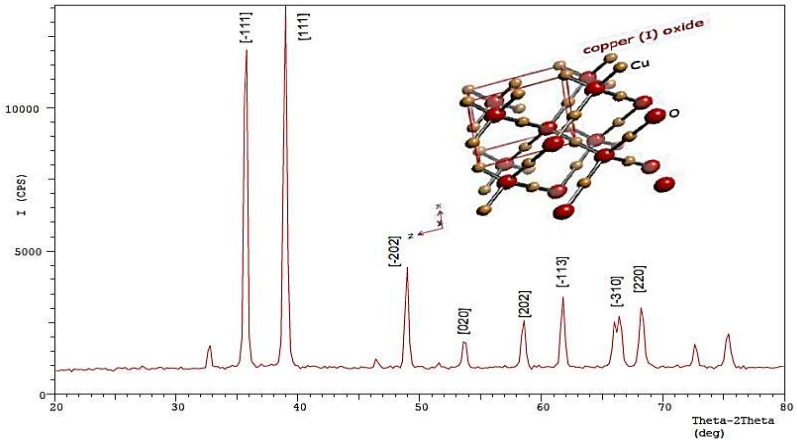

Fig. 1. XRD pattern of prepared CuO nanoparticles.

3.2. Infra-red Fourier transformation analysis (FT-IR)

In order to be sure of the chemical and structural nature of the material, FT-IR spectroscopy analysis has been done. CuO nanoparticles prepared in both methods has been scanned from 4000 cm^{-1} to 400cm^{-1} as shown in Fig. (2). It can be noticed two active peaks in the range of 400 to 600 cm^{-1} which corresponding to stretching vibrations of CuO bond in the monoclinic CuO[9].

Absorption bands in the range (1300 and 2000 cm^{-1}) are mainly attributed to the chemisorbed and/or physisorbed H_2O and CO_2 molecules that may attached on the surface of nano-structured CuO crystals[10]. Furthermore the absence of absorption peak at 610 cm^{-1} confirms that the synthesized product is pure CuO and may attributed to Cu_2O infrared active mode [11] .

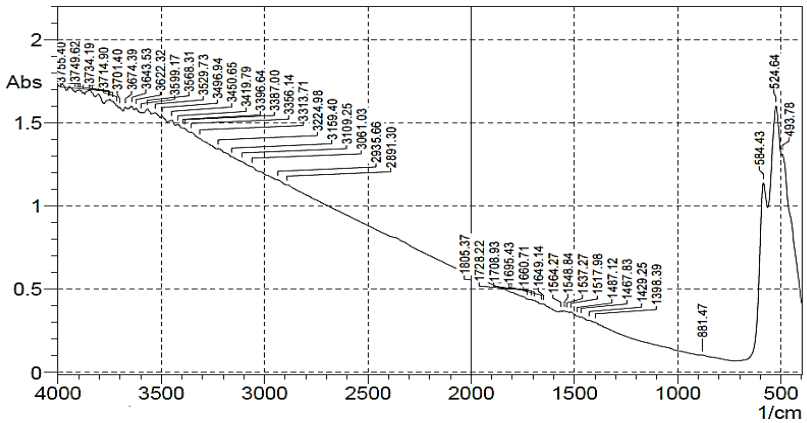

Fig. 2. FT-IR Spectrum of prepared CuO nanoparticles.

3.3. Morphology of Copper Oxide (SEM)

CuO-NPs prepared by both strategies (i.e. precipitation and sol-gel methods) and the size of the produced CuO nanoparticles has been investigated by SEM with different magnifications shown in Fig. (3 and 4) respectively. It can be noticed that there is difference in CuO structure since it tends to be more spherical with quasi architectural by precipitation method with homogeneous distribution and small agglomeration. In the present work copper acetate monohydrate ($Cu(CO_2CH_3)_2.H_2O$) has been used to prepare CuO nano particles with spherical shape via prescepitation method, the same morphology has been obtained using $Cu(NO_3)_2.3H_2O$ as reported by Anandan *et al*. who reported synthesis CuO crystallites self-organized into spherical assemblies or ‘‘dandelions’’ with a puffy appearance [12] and Kannaki *et.al*.[13] who used $CuSO_4.5H_2O$ shows that how the CuO nanocrystals organized into spherical assemblies. With higher magnification on individual particle it appears like dandelion. Moreover copper (II) chloride that used to prepare CuO structure via sol gel is more like reef with more ability to be agglomerate.

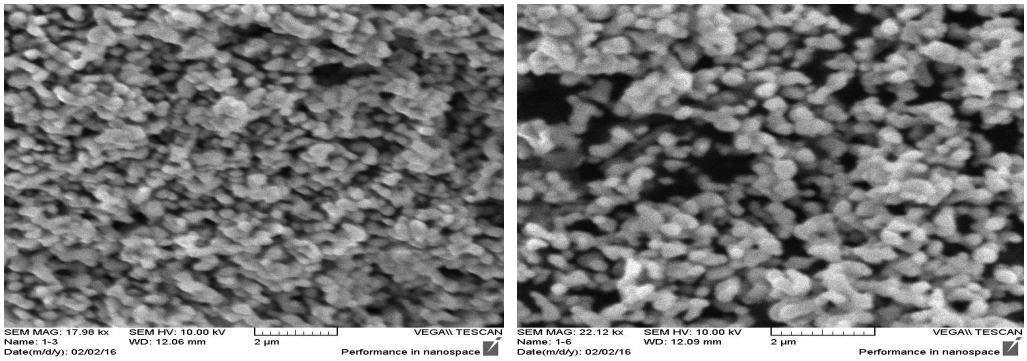

Fig. 3. SEM photographs of CuO nanoparticles prepared via **precipitation method.**

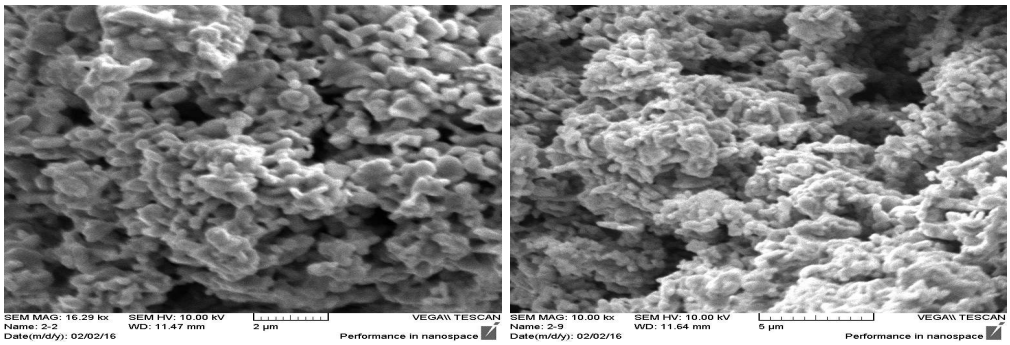

Fig. 4. SEM photographs of CuO nanoparticles prepared via Sol- Gel method.

4. Conclusion

Copper oxide can be synthesized using precipitation and sol- gel methods that were very efficient in producing small sized nanostructures(less than 2 µm). In this study, it has been noticed that the emergence of small nanoscale structures in various forms depending on the type of preparing and this makes it suitable for different applications. It wasobserved that shape, size, and homogeneity of the as-synthesized products depend uponvarious reactions conditions, i.e., the nature of the ligand, the relative concentration ofreagents, the solvent, the overall concentration of reagents, the reaction time, the evapo-ration time, and the reaction/evaporation temperature .

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تحضير تراكيب اوكسيد النحاس النانوية بطريقتي السول – جل والترسيب

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الخلاصة

تم تحضير التراكيب النانوية لاوكسيد النحاس بطريقتين مختلفتين، الطريقة الاولى هي طريقة الترسيب باستخدام خلات النحاس المائية $(CO_2CH_{13})_2.H2O$، وحامض الخليك الثلجي (CH_3COOH) وهيدروكسيد الصوديوم NaOH، والطريقة الثانية هي طريقة السول-جل باستخدام كلوريد النحاس $(CuCl_2)$ ، هيدروكسيد الصوديوم NaOH والايثانول (C_2H_6O). أظهرت نتائج المجهر الإلكتروني الماسح (SEM) تراكيب نانوية بأشكال مختلفة (كروية واخرى مرجانية الشكل) تكونت بطريقتي الترسيب والسول- جل على التوالي وحجم الجزيئات المتكونة كان اقل من ٢ مايكرون. وأظهرت نتائج جهاز حيود الأشعة السينية (XRD) عدم وجود شوائب التي قد تكون موجودة أثناء التحضير وحجم الجزيئات لاعلى قمة (٣٨.٩ درجة)، هو (١٥.٩٣نانومتر) وتم استخدام مطيافية الاشعة التحت الحمراء (FTIR) لمعرفة التركيب الداخلي لاوكسيد النحاس النانوي المحضر بنقاوة عالية اظهرتها قمة الامتصاص عند ٦١٠سم $^{-1}$.