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## **CuO nano particles synthesized via the mechanical method starting with solids state chemical reactions.**

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### **Abstract:**

Copper oxide nanoparticles have been prepared by the reductions of copper salts in the solid sodium hydroxide in the presence of salicylic acid as a catalyst and NaOH as stabilizing. The prepared nanoparticles were characterized using FT-IR spectroscopy, X-ray diffraction pattern, and scanning electron microscope, the synthesized copper oxide nanoparticles, have sizes in the range of (5-31)nm and layer thickness 6-9nm depending on the starting materials (copper salts).

### **1. Introduction**

Copper oxide nanoparticles is prepared by dry mechanical method using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with salicylic acid as a precursor and NaOH as stabilizing agent. This method gives large products of the nanoparticles. In the last decade, the metals nanosize materials and metal oxide particles are intensively attracted the attentions of researchers in different fields of applications. Transition metal oxides, CuO nanoparticles are used in the applications of storage devices, solar energy transfer, super capacitors, sensors and (1-2), ( etc).

Among the oxides of transition metals, CuO nanoparticles are of special interesting one because of their applications as nanofluid.(3), Copper oxide (CuO) nanoparticles synthesized by sol-gel(4-5) the borohydride reduction of copper nitrate salt can be used in optoelectronic devices (6), electrochemical cell (7), magnetic storage devices, gas sensors, super conductors, nanofluid and catalysts(8). The band gap of CuO nanoparticles around 2.6 eV. Therefore they can be used as solar cell window material. In this paper the CuO nanoparticles were synthesized by mechanical method(9), using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (gm) and salicylic acid and well mixed then. NaOH is added to the resulted solid mixture. grinding the solid materials. The colour of the solution changed from sky blue to black grinding then the products put in beaker with continuous stirring for 10 min. The black product was filtered and washed( 4) times with distilled water. (XRD). The size of the nanoparticles is estimated by XRD, scanning electron microscopy (SEM) and fourier transformation infra red (FTIR).

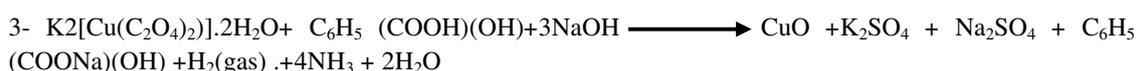
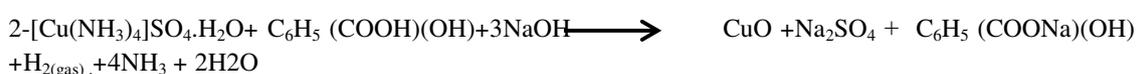
### **2. Materials and Methods:**



(1) gm Copper sulphate penta hydrate solid from (fluka), with (0.55) gm of solid salicylic acid(from BHD),were puted in porcelean mortar mixed together, no reactions between the two materials till the addition of (0.415) gm of solid NaOH(from fluka). The color of the solution changed from sky blue to black, the mechanical granding during 20 min then the products puted in buker contain distilled water with continuous stirring for 10 min. The black product was filtered and washed 4 times with distilled water, dried in air for three days. Also we prepared copper oxide nano particles from the following materials ).

[Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>.H<sub>2</sub>O and K<sub>2</sub>[Cu(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]. 2H<sub>2</sub>O , using the same procedure.

Applying the stehieometric equation:



This method is one of the most easy and low-cost ways to reduce mineral salts by a reducing agents. In mechanical methods, the temperature of the environment increases as the reaction progresses, and as a result, the particles become larger through the progress of the reaction. Among the chemical methods recovery is the best way to prepare nanoparticles. Mechanical chemistry is a branch of chemistry that studies the chemical changes of materials in solid situations using mechanical energy. The above definition is based on the theoretical results presented by Bacon(9) in his research the grinding is one of the most important instructions for active solid preparation. In heterogeneous ways, the reaction rate depends largely on the surface area of the solids being reacted, found that some soluble salts, when placed under mechanical pressure, lose water. It is also investigating the chemical process of silver chloride.

In general, the grinding of two solid particles give new compounds, produced due to the change in the crystalline structure resulted from the application of mechanical energy. These changes are created by creating gap energy between particles forming a new levels. The formation of new surfaces leads to new order of the crystalline molecules and leads to a breakage of the bond. After this stage, the formation of new compounds is a deformation of the crystals and a series of chemical reactions occure ,with the mechanical reaction steps as follows:

- 1-Crushing molecules into very fine particles.
- 2-Create new surfaces between particles by corrosion.
- 3- The formation of point defects in the structure of the crystal.

4- Change the middle shapes in multidimensional crystalline situations.(7-10)

Simplicity of environmental safety and product operation with high efficiency

The possibility of a clean environment due to the elimination of the use of solvents.

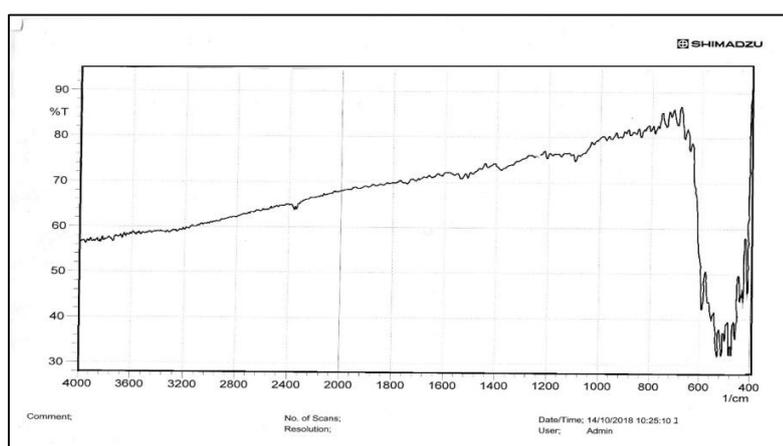
Minimize the number of processing steps, the possibility of achieving a semi-sustainable state, unlike other traditional methods of chemical reactions such as decomposition, ion exchange, reduction of oxidation, formation of new compounds(10-13).

### 3. Results and discussions:

The CuO nanoparticles were characterized by studying their structure by X-ray diffraction (XRD). The size of the nanoparticles is estimated by XRD, Scanning electron microscopy (SEM) and fourior transformation infra red (FTIR).FT-IR spectrum which is

#### 3.1. FTIR

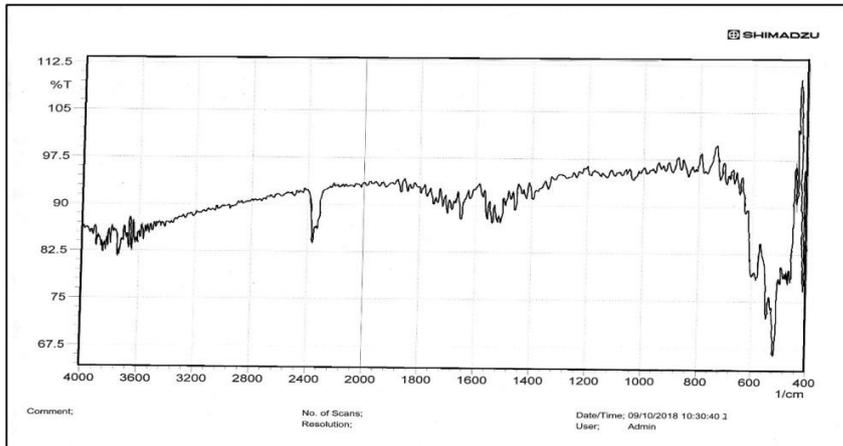
shown in Figure 1 confirms the formation of copper oxide nanoparticles. The existence of absorption peaks at wavenumbers of more than  $600\text{ cm}^{-1}$  in the sample indicated that the covalent bonds existence from organic sources from salisylic acid. The absorption peaks at wavenumbers  $3428$ ,  $2917$ , and  $1652\text{ cm}^{-1}$  coresponding to N–H, C–H, and C=O stretching vibrations, respectively Furthermore, the absorption peak appeared at  $1428\text{ cm}^{-1}$  refer to the vibration caused by C–H bending in the methylene group in the salsylic acid, while the band at  $1272\text{ cm}^{-1}$  was related to C–N stretching vibration. Ultimately, the bands containing peaks at  $836$  and  $631\text{ cm}^{-1}$  were attributed to  $\text{NO}_3^-$  groups



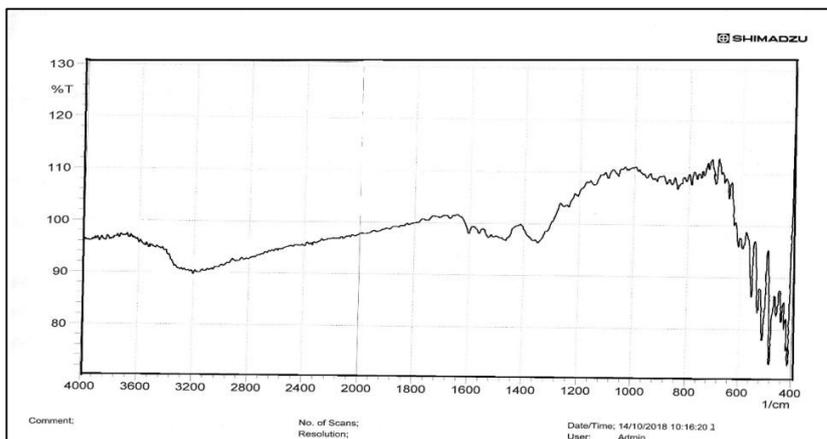
**Fig. (1) FTIR spectrum of CuO nano particles prepared from CuSO<sub>4</sub>.5H<sub>2</sub>O**

vibrations, the peaks which appear in the range of  $706\text{--}912\text{ cm}^{-1}$  that might be due to

bending mode of vibrations M–O–M bending (M=Cu)(14-16) there is no differences in the FTIR spectrums with the used precursor starting materials.



**Fig. 2. FTIR spectrum of CuO nano particles prepared from  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$**



**Fig. ( 3) FTIR spectrum of CuO nano particles prepared from  $\text{K}_2[\text{Cu}(\text{OX})_2] \cdot 2\text{H}_2\text{O}$**

### 3.2. XRD:

The CuO nanoparticles were characterized by studying their structure by X-ray diffraction. X-ray diffraction studies have been carried out using Analytical x-ray diffractometer and surface morphology of the samples has been studied using scanning electron microscope (JEOL JSMS 800-V). Compositional analysis of the samples has been studied using energy dispersive analysis of X-rays (JEOL Model JED -2300) ones

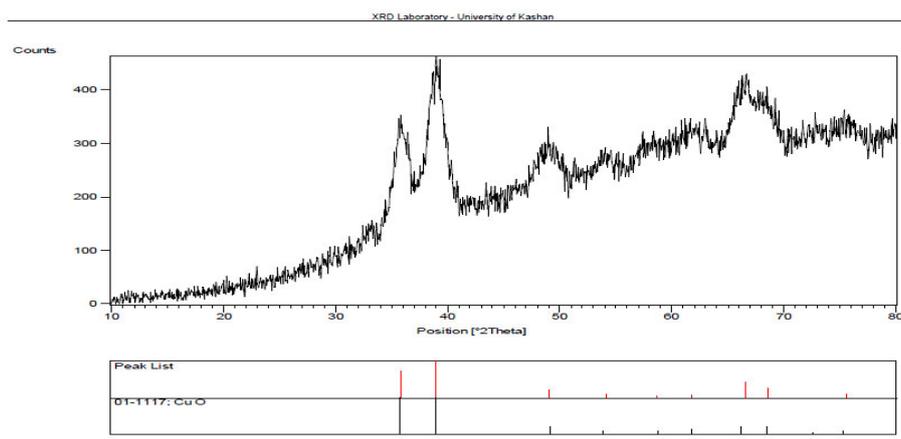


Fig.(4) XRD pattern OF Cuper oxide nano particle shows the calculated particle size 6.687nm

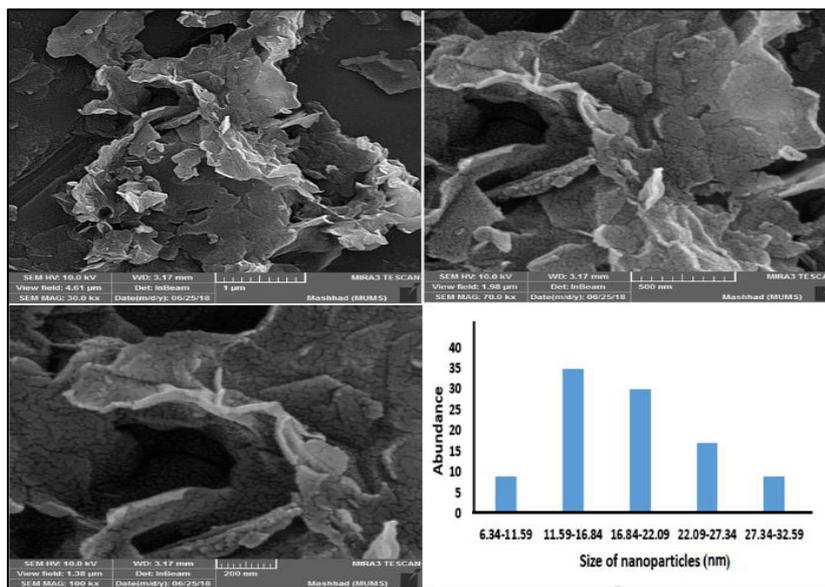
corresponding to the (111), (200) and (220) planes of copper.

This from the preparations of CuO nano particles from the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

The Fig. 4. X-ray diffraction pattern of copper nanoparticles. Shows the peaks belongs to the plan (111) is at (43.473 eV), the peak which corresponding to the plan (200) is at (50.375 eV), the plan (220) is at (73.997 eV) and the plan (311) at (89.934 eV) these planes belong to the fcc metallic Cu (JCPDS, PDF, File No. 00-001-1241). The peaks belong to  $\text{Cu}_2\text{O}$  (JCPDS, PDF, File No. 01-071-3645), confirme that  $\text{Cu}_2\text{O}$  also coexists partly together with copper particles. The coexisting  $\text{Cu}_2\text{O}$  is because some oxidation process in air. Figure 3 shows that the sample has a crystalline structure. The XRD patterns reveal two main peaks at  $2\theta = 36.1^\circ$  and  $2\theta = 39^\circ$  that can be ascribed to the (-111) and (111) plan diffractions of the CuO phase (12). The average crystallite size of the nanolayer of CuO is about 6.0 nm calculated by using Debye-Scherrer formula. The lattice constant of the unit cell is  $a = 4.6965 \text{ \AA}$ ,  $b = 3.4324 \text{ \AA}$  and  $c = 5.1329 \text{ \AA}$ ,  $\beta = 99.5287^\circ$  (11). It was found to be highly crystalline. The diffraction is in good coordination with ASTM card no. 74-1021. [17-19]

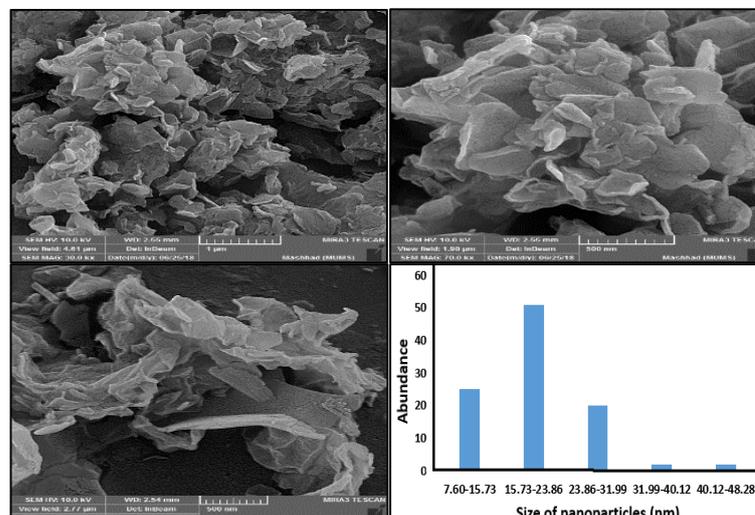
### 3.3 Scanning electron microscopy SEM:

The morphology of the CuO nano particles was cluster, the synthesized CuO are shown in the fig. 5. It is quite evident that there is no definite morphology in the sample. It seems that the particles were agglomerated and form a cluster. The morphology observed in the sample not showing any hard grains which gives the idea that the size of the particle is small (20)



Fig, 5 shows SEM the morphology and the distributions of the nano particles using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in the preparations of CuO nano particles.

From the SEM image we choose 100 points treated by the soft wear dymizer we



get the histogram of distributions of the CuO nano particles it is founds that 35% of the particles are in the range of (11.59-16.84)nm and 30% of the particles are in the size in the range between( 16.09- 22.09) nm (21 ) when the CuO nano particles prepared with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Fig. 6 shows SEM the morphology and the distributions of the nano particles using  $\text{Cu}(\text{NH}_3)_4 \cdot \text{H}_2\text{O}$  in the preparations of CuO nano particles.

Fig 6 shows that 50% of the particles are in sizes ranging between (15.73-23.86)nm and 25% of the particles are in the size in the range between ( 7.6 – 15.73 ) nm (16-17) when the CuO nano were synthesized from  $\text{Cu}(\text{NH}_3)_4 \cdot \text{H}_2\text{O}$

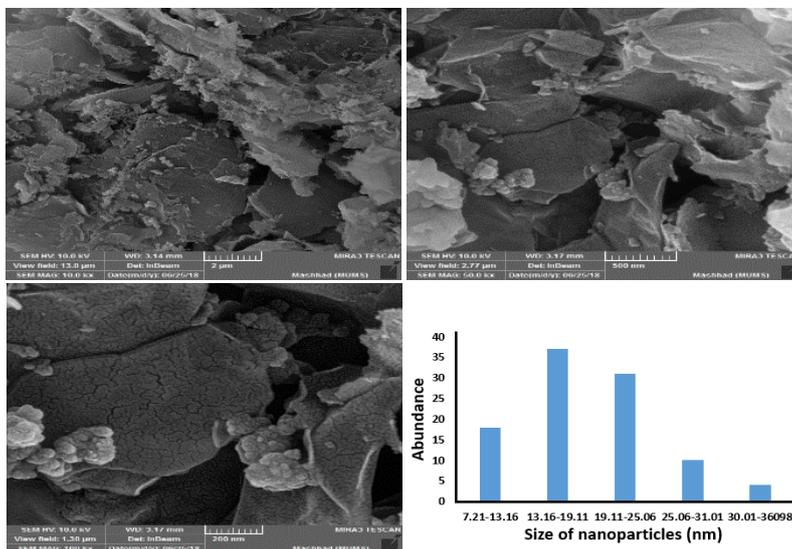


Fig. 7 shows SEM the morphology and the distributions of the nano particles using  $\text{K}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  in the preparations of CuO nano particles. Found that the particles sizes of 35% in the range of (13.16-19.11) nm, 30% of the particles size are in the range of (19.11-25.06) nm and 15% in between (7.21-13.16)nm.

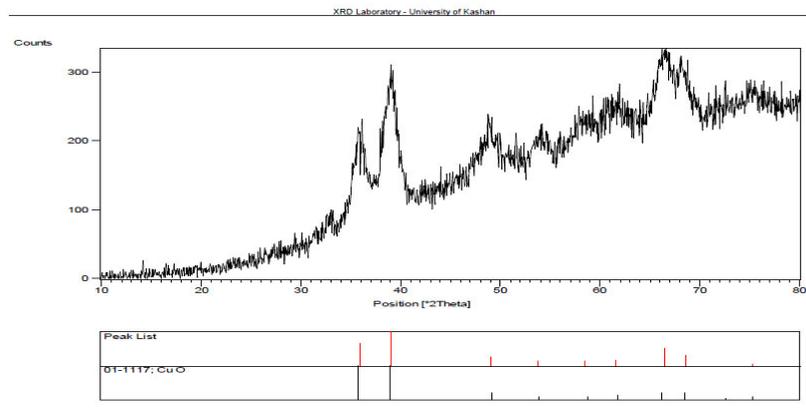


Fig.8 xrd pattern shows the nano particles prepared using the  $\text{CuO}(\text{NH}_3)_4 \cdot \text{H}_2\text{O}$  calculating the particles size using the Debye–Scherrer formula found 8.499nm,

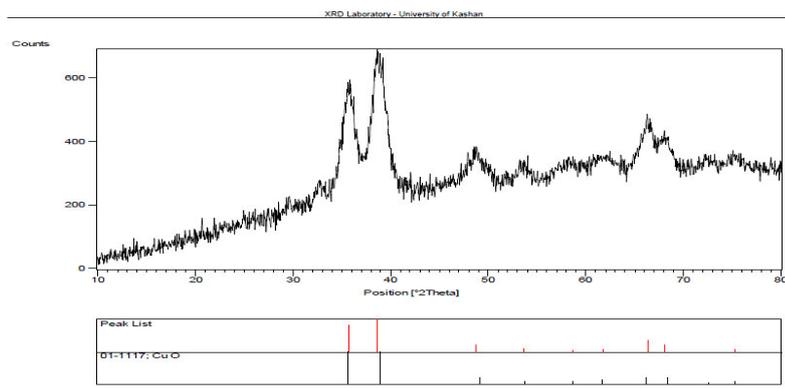


Fig. 9 xrd pattern shows the nano particles prepared using the  $\text{Cu}(\text{C}_2\text{O}_4)_4 \cdot \text{H}_2\text{O}$  calculating the particles size using the Debye–Scherrer formula found 7.729 nm.

#### 4. Conclusions:

Nanoparticles of CuO were produced by the mechanical method. Also, the nanolayers of CuO using the mechanical technique. The structure and morphology of the nanoparticles are nanolayers were characterized by XRD spectroscopy, and SEM and FTIR techniques. It was found that the particles size rang arebetween 6-9 nm depending on the starting copper salts at room temperature.

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