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The effect of solvents on the size of copper oxide particles fabricated using photolysis method

Zaid Hamid Mahmoud*, Nuha Farhan Abdul Kareem, Aklas Ahmed Abdul Kareem

Department of Chemistry, Collage Science, Diyala University, Iraq

Abstract : Copper oxide nanoparticles with different size were successfully fabricated by the photolysis method through the irradiation of copper oxalate complex with different solvents. The effect of the type of solvent on the size of nanoparticles was investigated. The structure and size of nanoparticles were determined using XRD and TEM while, the spectra properties of it investigated using FTIR and UV-Vis. XRD diffraction studies obtained pure monoclinic structure of copper oxide without secondary phase and the size of particles (8.4 to 11.4nm) depends strongly on the dielectric constant of solvents and the smallest particles of copper oxide were showed when using the ethanol as solvent. A blue shift in the essential gap energy (from 4.21 to 4.58eV) due to the quantum confinement effect, is obtained in the spectra analysis when the particles size decreases.
Key words : CuO, nanoparticles, photolysis, irradiation, quantum confinement.

Introduction

Inorganic nanostructures materials with fully-determined morphologies having excellent properties and probable applications have received major attention in recent years.The nanoparticles of metal oxide are very paramount in inorganic material research for developing different practical applications andthese nanoparticles have individual chemical properties [1-3] depends powerfully on their structure, composition, shape, and size [4-6].Copper oxide NPs are the most studied materials between all the metal oxides because of interesting properties as a p-type semiconductor with the possibility of a large difference in energy band gap.Copper oxide are used in many different applications such as nanofluid[7], gas sensors [8], anodes in battery [9], magnetic storage media [10], photodetectors[11], energetic materials [12], photocatalysis[13], antibacterial materials [14], and many others.Through the past few years, several methods used to fabricate the copper oxide NPs including sol gel [15], hydrothermal [16], sonochemical[17], microwave [18], and solvothermal[19]. Of all the above synthesis procedure, it appears to be very difficult to get a pure crystal of copper oxide material without adding many stabilizing agents. Actually, as it was adduced [20], the elaboration of copper oxide NPs is usually accompanied by the presence of side product such Cu_2Oor $Cu(OH)_2$.For this, the defy taken up in this paper is to fabricate pure CuO NPs, in the nano range, using novel and the low-cost photolysis method without adding any stabilizing agent. This process contained irradiation the complex or salt of copper to transform it from the double oxidation state (+2) to oxidation state (+1) using an ice bath to avoid the high temperature then, the product burned at 300C.furthermore, as it can be abstracted from this work when the fabricate parameters are well optimized, the photolysis method can produce a pure product. In this framework, the paper aim too to study the effect of the solvent nature on the size of particles of the as-prepared CuO NPs.

Experimental

Copper oxide NPs were prepared using potassium oxalate and copper sulphate (sigma Aldrich, 99%) as precursors.

2.1 preparation of complex and CuO NPs

In two separate beakers, 3.1gm of potassium oxalate monohydrate and 2.0gm of copper sulphate pent hydrate were dissolved with stirring in 15ml and 10ml distilled water respectively. Next, the oxalate and copper solutions were mixed together with continuous stirring and heated at 60C for 30min and then it cooled in ice water bath until blue crystal appeared. The crystals were washed with acetone and dried at room temperature. After that, three quantities of oxalate complex (2.0gm) were, separately, dissolved in 70ml of different solvents (water, ethanol and methanol) and irradiated using irradiation system (fig. 1)for 2hours. Brown precipitate was appeared during irradiation the three solutions, then it separated and washed with acetone and burned at 400C for 30min. black precipitate from copper oxide was appeared.

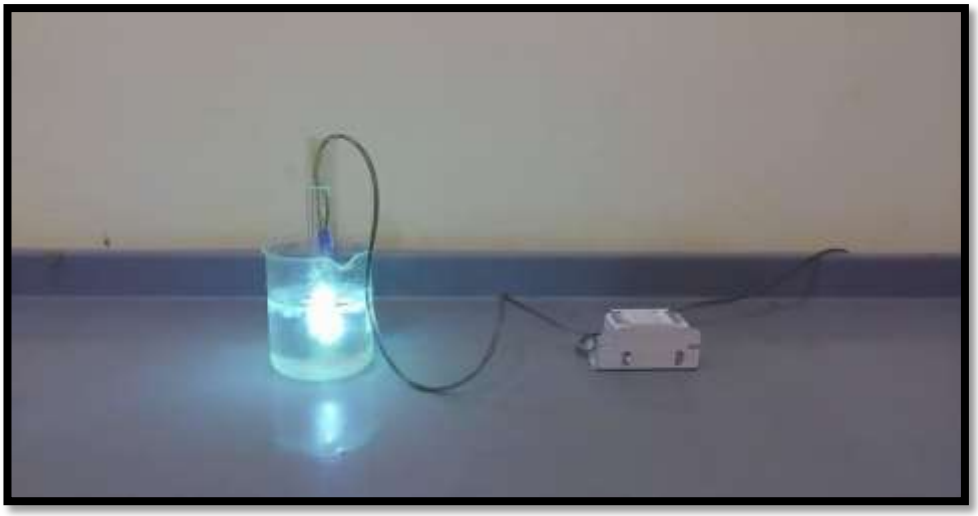


Fig. 1, Theirradiation system

2.2 Characterization

The identity and structure of the particles were determined using a XRD(XRD-6000) with copper Kαradiation. FTIR spectrum of copper complex and oxide recorded on a Four or transform Infrared Spectrophotometer ShShimadzu while, the UV spectrum of nano oxides measured using a Spectrophotometer. the morphology and size of particles were recorded by a TEM (JEOL JEM-2100 Japan).

Result and discussions

The XRD patterns of as-prepared complex and nanoparticles of copper oxide using different solvents are shown in fig 2. From patterns recorded, the complex crystallized in the orthorhombic system while, monoclinic for copper oxides and it's in good agreement with JCPDS card No: 210297 and 0481548 respectively. Depending on the nature of solvents, the diffraction of patterns appears boarding linked with the lattice strain and crystallite size. By using Scherr formula, the size of copper oxides found and equals to 11.4nm, 10.8nm and 8.4nm when using water, methanol and ethanol respectively.

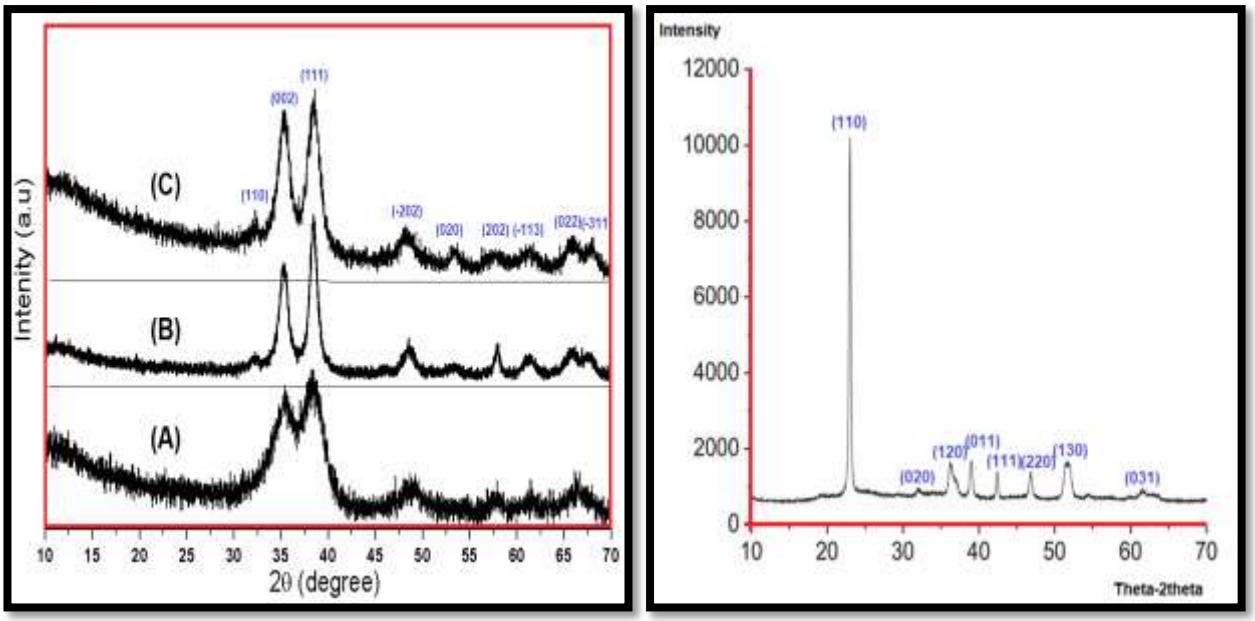
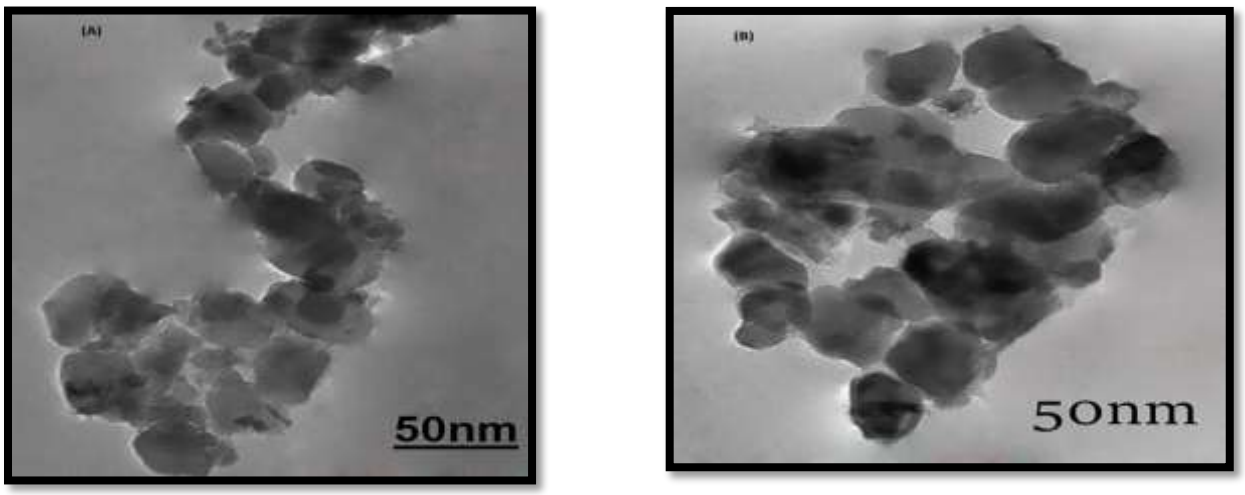


Fig. 2: XRD spectrum of CuO NPs prepared using ethanol as solvents (A), methanol (B), water (C) and spectrum of copper oxalate (D)

The TEM images of the as synthesized copper oxide NPs in different solvents are showed at fig (3a-c). The size of particles depended strongly on the nature of solvents used and the result is in agreement with the XRD results. From result observed that the decrease in dielectric constant for the solvent led to a decrease in the size of particles. The mechanism of growth the particle depended on ΔG barrier that needed to make a homogenous nucleus able to grow spontaneously. This energy is inversely proportional to ΔG^2 and G proportional to the S (super saturation) and it equal to ionic product divided by solubility. Where fore it decrease the solubility product of compound by decreasing the dielectric constant of solvents, increase S and finally, make the formation of homogenous nuclei easier. At the end, obtain a higher number of homogenous nuclei a higher number of particles due to the decrease in dielectric constant of the solvents. For a given quantity to precipitate, the particles will be then smaller, because this quantity will be divided by a greater number of particles.[21-23]



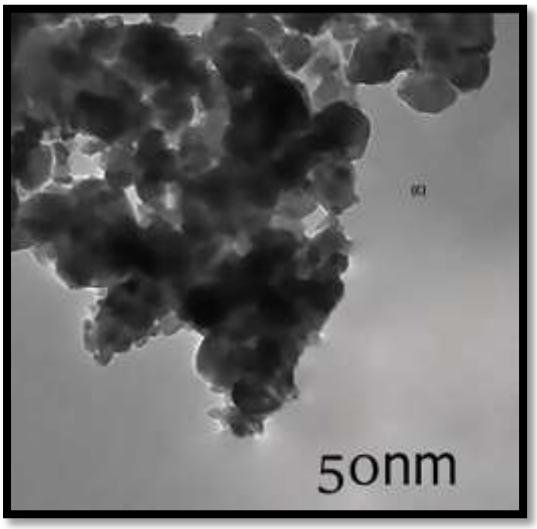


Fig. 3 : The images of TEM for CuO NPs prepared using ethanol as solvents (A), methanol (B), water (C)

FTIR spectrum of copper complex and its oxides were shown at fig (4a, b). several types of vibration showed at fig (4a) centered in 1649cm^{-1} and 1675cm^{-1} assigned to C=O groups and strong band located at 490cm^{-1} back to Cu-O while, three bands showed at fig (4b) centered at 637, 522 and 600cm-1 assigned to symmetric, asymmetric starching and wagging vibration for Cu-O.

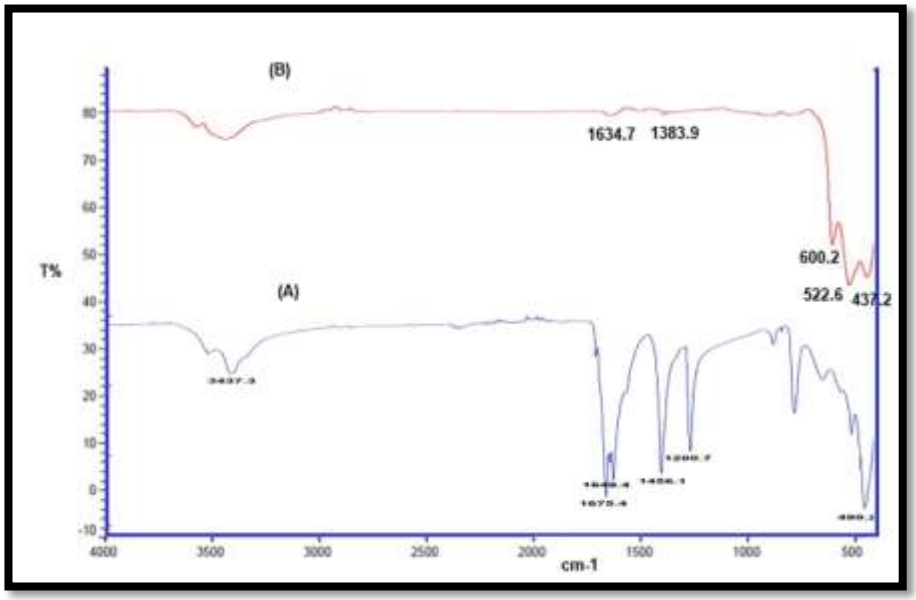


Fig. 4: FTIR spectrum of copper oxalate complex (A) and copper oxide NPs (B)

The adsorption spectra of copper oxides prepared using (water, methanol and ethanol) as solvents showed in fig (5). All samples appeared a maximum absorption peak at about 262, 268 and 285nm when using ethanol water, methanol and as solvents respectively.

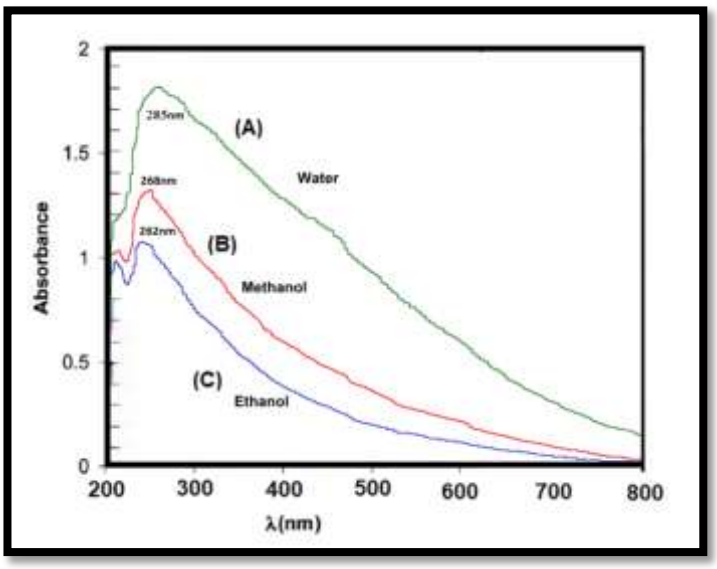


Fig. 5: UV-Vis of CuO NPs prepared using water as solvents (A), methanol (B), ethanol (C)

The energy gap of samples of copper oxide synthesized using photolysis method was determined (table 1) using spectrum of UV-Visby edge of absorption of nanoparticles from the formula:

Eg = 1240/□max

A blue shift appeared in energy with decreasing the size of particles due to the quantum confinement effect[24, 25] and the exaction Bohr radius, corresponds to a principal shift in optical and electronic properties.[26]

Table 1: the value of gap energy for copper oxide NPs syntheses in different solvents

sample	solvents	Particle size	λ max	Energy gap
CuO	water	11.4	285	4.21
CuO	methanol	10.8	268	4.47
CuO	ethanol	8.4	262	4.58

Conclusion

The crystal of CuO nanoparticles, ranging from 8.4 to 11.4 nm, were prepared using photolysis method, without adding any stabilizing agent. The effect of solvent on the size, and optical properties of CuO NPs was studied. Single without secondary phase of monoclinic copper oxide NPs, were investigated by XRD. However, TEM discovers that the size of the prepared nanoparticles changes according to the solvent due to the change is attributed to the dielectric constant of the solvent. Moreover, the measured values of band gap for the prepared copper oxide nanoparticles indicated a blue shift because of the quantum confinement effect.

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