

Effect of Solvents on Size of Copper Oxide Nanoparticles Fabricated using Photolysis Method

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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 spectral properties of copper oxide nanoparticles investigated using FTIR and UV-visible. XRD diffraction studies obtained pure monoclinic structure of copper oxide without secondary phase and the size of particles (8.4 to 11.4 nm) 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 4.58 eV) due to the quantum confinement effect, is obtained in the spectra analysis when the particles size decreases.

Keywords: Copper oxide 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 prominent in inorganic material research for developing different practical applications and these nanoparticles have individual chemical properties [1-3] depends on their structure, composition, shape and size [4-6]. Copper oxide nanoparticles 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 nanoparticles 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 nanoparticles is usually accompanied by the presence of side product such Cu₂O or Cu(OH)₂. For this, the defy taken up in this paper is to fabricate pure copper oxide nanoparticles, 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 oxidation state (+2) to oxidation state (+1) using an ice bath to avoid the high temperature then, the product burned at 300 °C. 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 to study the effect of the solvent nature on the size of particles of the as-prepared copper oxide nanoparticles.

EXPERIMENTAL

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

Preparation of complex and copper oxide nanoparticles: In two separate beakers, 3.1 g of potassium oxalate monohydrate and 2.0 g of copper sulphate penta hydrate were dissolved with stirring in 15 and 10 mL distilled water respectively. Next, the oxalate and copper solutions were mixed together with continuous stirring and heated at 60 °C for 30 min 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 (2.0 g) were, separately, dissolved in 70 mL of different solvents (water, ethanol and methanol) and irradiated using irradiation system for 2 h. Brown precipitate was appeared during irradiation of the three solutions, then it separated and washed with acetone and heated at 400 °C for 30 min. A black precipitate from copper oxide was appeared.

Characterization: The identity and structure of the particles were determined using a XRD (XRD-6000) with CuK_{α} radiation. FTIR spectrum of copper complex and oxide recorded on a Fourier transform infrared spectrophotometer Shimadzu while, the UV spectrum of nanoparticles measured using a spectrophotometer. The morphology and size of particles were recorded by a TEM (JEOL JEM-2100 Japan).

RESULTS AND DISCUSSION

The XRD patterns of as-prepared complex and nanoparticles of copper oxide using different solvents are shown in Fig. 1. 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 11.4, 10.8 and 8.4 nm when using water, methanol and ethanol respectively.

The TEM images of the as synthesized copper oxide nanoparticles in different solvents are showed at Fig. 2(a-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. 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 then be smaller, because this quantity will be divided by a greater number of particles [21-23].

FTIR spectrum of copper complex and its nanoparticles were shown at Fig. 3(a,b). Several types of vibration showed at Fig. 3(a) centered in 1649 and 1675 cm⁻¹ assigned to C=O groups and strong band located at 490 cm⁻¹ back to Cu-O while, three bands showed at Fig. 3(b) centered at 637, 522 and 600 cm⁻¹ assigned to symmetric, asymmetric stretching and wagging vibration respectively for Cu-O.

The adsorption spectra of copper oxides prepared using (water, methanol and ethanol) as solvents showed in Fig. 4. All samples appeared a maximum absorption peak at about 262, 268 and 285 nm when using ethanol water, methanol and as solvents respectively.



Fig. 1. XRD spectrum of copper oxide nanoparticles prepared using ethanol as solvents (A), methanol (B), water (C) and spectrum of copper oxalate (D)



Fig. 2. TEM images for copper oxide nanoparticles prepared using ethanol as solvents (A), methanol (B), water (C)



Fig. 3. FTIR spectrum of copper oxalate complex (A) and copper oxide nanoparticles (B)



Fig. 4. UV-visible of copper oxide nanoparticles prepared using water as solvents (A), methanol (B), ethanol (C)

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

$$E_g = 1240/\lambda_{max}$$

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				
VALUE OF GAP ENERGY FOR COPPER OXIDE				
NANOPARTICLES 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 copper oxide nanoparticles, ranging from 8.4 to 11.4 nm size were prepared using photolysis method, without adding any stabilizing agent. The effect of solvent on the size and optical properties of copper oxide nanoparticles was studied. Single without secondary phase of monoclinic copper oxide

nanoparticles, 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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